

PRIMARY PRODUCTIVITY IN OIL REFINERY  
EFFLUENT-HOLDING PONDS

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PRIMARY PRODUCTIVITY IN OIL REFINERY  
EFFLUENT-HOLDING PONDS

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## TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION. . . . .	1
II. REVIEW OF THE LITERATURE. . . . .	4
III. METHODS AND PROCEDURE . . . . .	6
Methods of Collection and Analysis of Samples. . . . .	6
Measurement of Community Metabolism. . . . .	6
Measurement of Day-Net Productivity. . . . .	8
IV. RESULTS AND CONCLUSIONS . . . . .	9
Gross Primary Productivity . . . . .	9
Community Respiration. . . . .	12
Day-Net Productivity . . . . .	14
Discussion . . . . .	14
V. SUMMARY . . . . .	16
SELECTED BIBLIOGRAPHY . . . . .	17
APPENDIX. . . . .	19

## LIST OF TABLES

Table	Page
I. The Dissolved Oxygen Concentration in mg/liter and the Per Cent Saturation at Refinery A . . . . .	20
II. The Dissolved Oxygen Concentration in mg/liter and the Per Cent Saturation at Refinery B . . . . .	22
III. Summary of the Community Metabolism Determined from Diurnal Rate-of-Change Curves (Figures 7 to 20) . . . . .	24
IV. The Per Cent Efficiency of the Ability of Algae in Oil Refinery Ponds to Convert Visible Solar Radiation into Carbohydrates. . . . .	25
V. Day-Net Productivity as Calculated from Daily Maximum and Minimum Oxygen Concentrations . . . . .	26

## LIST OF FIGURES

Figure	Page
1. A Diagram of the Effluent-Holding Ponds and Sampling Locations at Refinery A . . . . .	27
2. A Diagram of the Effluent-Holding Ponds and Sampling Locations at Refinery B . . . . .	28
3. A Typical Diurnal Curve and Calculation for Gross Primary Productivity (Pg), Community Respiration (R), and Diffusion Constant (k). . . . .	29
4. Regression of Community Respiration (R) and Gross Primary Productivity (Pg) at Refinery A . . . . .	30
5. Regression of Community Respiration (R) and Gross Primary Productivity (Pg) at Refinery B . . . . .	31
6. Regression of Day-Net Productivity for Refinery A and B . . .	32
7. Diurnal Oxygen Curve for Holding Pond #1 (21.4 days holding time) at Refinery A . . . . .	33

# LIST OF FIGURES (Continued)

Figure	Page
8. Diurnal Oxygen Curve for Holding Pond #2 (23.5 days holding time) at Refinery A . . . . .	34
9. Diurnal Oxygen Curve for Holding Pond #3 (26.2 days holding time) at Refinery A . . . . .	35
10. Diurnal Oxygen Curve for Holding Pond #4 (30.4 days holding time) at Refinery A . . . . .	36
11. Diurnal Oxygen Curve for Holding Pond #5 (33.5 days holding time) at Refinery A . . . . .	37
12. Diurnal Oxygen Curve for Holding Pond #6 (37.0 days holding time) at Refinery A . . . . .	38
13. Diurnal Oxygen Curve for Oil Pond #3 (16.4 days holding time) at Refinery B . . . . .	39
14. Diurnal Oxygen Curve for Oxidation Pond #2 (17.9 days holding time) at Refinery B . . . . .	40
15. Diurnal Oxygen Curve for Bay 1 of Oxidation Pond #3 (20.0 days holding time) at Refinery B. . . . .	41
16. Diurnal Oxygen Curve for Bay 2 of Oxidation Pond #3 (26.0 days holding time) at Refinery B. . . . .	42
17. Diurnal Oxygen Curve for Bay 3 of Oxidation Pond #3 (31.0 days holding time) at Refinery B. . . . .	43
18. Diurnal Oxygen Curve for Bay 4 of Oxidation Pond #3 (37.0 days holding time) at Refinery B. . . . .	44
19. Diurnal Oxygen Curve for Bay 1 of Oxidation Pond #4 (48.0 days holding time) at Refinery B. . . . .	45
20. Diurnal Oxygen Curve for Bay 3 of Oxidation Pond #4 (60.4 days holding time) at Refinery B. . . . .	46

## CHAPTER I

### INTRODUCTION

During the process of photosynthesis, light energy is used by green plants to synthesize carbon-containing organic materials from carbon dioxide as represented in the illustration;



The light energy is incorporated by chlorophyll into 3-phospho-glyceric acid which is converted into the components of protoplasm. Since one gram of oxygen is liberated for approximately each gram of carbohydrate produced, a measurement of the oxygen production is an indirect estimate of the rate at which energy is stored by photosynthetic processes. The rate at which green plants produce carbohydrates is called primary productivity (Odum, 1959).

A comparative study of the primary productivity in effluent-holding ponds at two petroleum refineries was conducted in the summer of 1960. In agreement with the refiners, the names of the refineries are not disclosed here and the refineries studied are referred to as Refinery A and Refinery B. Refinery A is located in southwestern Oklahoma and Refinery B is located 230 miles to the northeast of Refinery A.

At Refinery A, there was a series of nine ponds, each separated by a submerged pipe (Figure 1). The ponds were arranged so that the water going into the end of one pond must travel to the opposite end to enter the next. All nine ponds, which the refiners called "Holding Ponds,"

were approximately five feet in depth. The last six ponds supported algal populations, while the first three did not. These first three ponds were characterized by the absence of free oxygen. About 37 days was required for the water to travel from the beginning to the end of the pond system.

The effluent at Refinery B passed first through a series of three ponds, about 14 feet deep, called "Oil Settling Ponds". The effluent then passed to four shallower ponds about five feet deep called "Oxidation Ponds" (Figure 2). Water flowed from pond to pond through submerged pipes. However, in Oxidation Pond Number 3, dikes had been constructed to separate the pond into four bays. Oxidation Pond Number 4 was separated into three bays. The first two oil settling ponds did not support algal populations and were anaerobic in the sense that they contained no free oxygen. Time required for passage of the effluent through the entire system was about 60 days. Water level in the ponds and chemical characteristics at each station remained relatively constant throughout the period of study at both refineries.

The refining processes at Refinery A included crude distillation with light naphtha specialties, vacuum distillation, catalytic cracking, and polymerization. At Refinery B, the refining processes included crude distillation, vacuum distillation, catalytic cracking, HF alkylation, propane deasphalting, and catalytic reforming.

Refinery effluents have a high organic matter concentration. Bacterial decomposition of organic matter results in the release of carbon dioxide. In aquatic situations, the carbon dioxide may be used by algae and other plants in the process of photosynthesis.

The size of any population is influenced by the amount of nutrients



available. Waste waters of high organic content such as domestic sewage, papermill wastes, cannery wastes, and oil refinery wastes may be expected to support large algal populations. As the quantity of organic material is decreased by bacterial activity there may be a corresponding decrease in the available carbon dioxide and in the associated algal populations.

## CHAPTER II

### REVIEW OF THE LITERATURE

The first concept of indirect measurement of phytoplankton production was advanced by Atkins (1922) of the United Kingdom. He based his estimates on the uptake of carbon dioxide from the water.

Manning and Juday (1941) made observations on the concentration and distribution of chlorophyll in several Wisconsin lakes. They estimated primary productivity by the oxygen change in light-and-dark bottles and correlated the productivity with the amount of chlorophyll present. At optimum light intensity it was found that the average productivity rate was seven milligrams of oxygen produced per milligram of chlorophyll per hour. It is now believed (Odum and Hoskin, 1958) that light-and-dark bottle measurements are insufficient to determine the community metabolism because they measure only the production of the suspended phytoplankton.

The work of Lindeman (1942) provided the basis for the concept of primary productivity. He indicated that a biotic community cannot be clearly differentiated from its abiotic environment, and together they form an ecosystem. The productivity of each level (producers, primary consumers, secondary consumers, decomposers, etc.) was defined as the rate at which energy was incorporated.

Odum and Odum (1955) measured the primary productivity and community respiration of a coral reef in the Pacific Ocean. A diurnal rate-of-change in oxygen concentrations between two stations was used to estimate the primary productivity. The primary productivity estimate of 24

gm/M<sup>2</sup>/day was considered to be high because no correction for diffusion was made. It was not until the following year that a method of correcting for diffusion was developed (Odum, 1956, 1957a and 1957b).

Verduim (1956) computed estimates of primary productivity for Western Lake Erie and some Colorado lakes by using standing crop data, that was measured in situ, and photosynthetic values obtained under laboratory conditions. He obtained values of the same order of magnitude that Manning and Juday (1941) obtained on the Wisconsin lakes. Goldman (1960) observed lower values in three lakes on the Alaskan Peninsula by using the tagged carbon technique.

Odum (1956) included a summary of the published data that would lend itself to the diurnal method of measurement. In less than 25 instances in the literature were there adequate data for diurnal rate-of-change analyses. All of these values were corrected for diffusion to yield more accurate productivity estimates. The highest productivity estimate reported occurred in a polluted river in Indiana. It was concluded that organic pollution may cause higher primary productivity.

Odum and Hoskin (1958) reported primary productivity estimates of a number of stations on the Texas coast in which the diurnal curve method of analyses were used. At one sampling station (Redfish Bay) there was some sewage pollution and a higher primary productivity.

Most of the oxygen measurements made on organically polluted waters have been limited to the usual eight-hour (daylight) working day (Bartsch, 1960) and the low point which may have occurred during the night was not detected. Oswald, et al. (1957) defined production in sewage ponds as the difference between the maximum and minimum daylight oxygen concentrations. This method gave no indication of the oxygen used in respiration or of diffusion losses or gains.

## CHAPTER III

### METHODS AND PROCEDURE

#### Methods of Collection and Analysis of Samples

Collection stations were established at the outlet of each pond and bay as shown in Figures 1 and 2. Six series of samples were taken at Refinery A and three at Refinery B between May 30 and September 1, 1960 (Tables I and II). Temperature and duplicate oxygen samples were obtained at each station at frequent intervals during a 24 hour period. Water samples for dissolved oxygen analyses were taken with a Kemmerer water sampler and immediately fixed by the Alsterburg (Azide) modification of the Winkler method (Barnes, 1959). Iodine liberated by the dissolved oxygen was measured colorimetrically with a Bausch and Lomb Spectronic 20 photoelectric colorimeter at a wave length of 450 millimicrons. The samples were measured soon after being fixed because in warm weather, the iodine color begins to fade after about six or seven hours. The milligrams of dissolved oxygen per liter were determined from a table converting the color measurement to milligrams per liter.

#### Measurement of Community Metabolism

The procedure outlined by Odum and Hoskin (1958) was followed in the measurement of primary productivity. An example of a hypothetical situation is given in Figure 3. Oxygen concentration and per cent oxygen saturation at each sample period were plotted against time in hours

(Figures 3 and 7 through 20).

The rate of oxygen change in milligrams per liter per hour (mg/l/hr) was determined from an oxygen concentration curve and plotted (Figures 3 and 7 through 20). Diffusion constant (k) in milligrams per liter at zero per cent saturation was determined from the rate of change curve and per cent saturation curve as follows;

$$k = \frac{q_m - q_e}{S_m - S_e} \quad \text{where}$$

$q_m$  is the rate of change at a predawn period in mg/l/hr.,

$q_e$  is the rate of change at a post sunset period in mg/l/hr.,

$S_m$  is the decimal saturation deficit at the time of  $q_m$ , and

$S_e$  is the decimal saturation deficit at the time of  $q_e$ .

The calculated diffusion constant for Figure 3 was;

$$k = \frac{q_m - q_e}{S_m - S_e}, \text{ or } \frac{0.00 - (-0.90)}{0.48 - (-0.48)}, \text{ or } \frac{0.90}{0.96}, \text{ or about } 1.0 \text{ mg/l/hr. or } 1.0 \text{ gram}$$

per cubic meter per hour (gm/M<sup>3</sup>/hr.) at 0 per cent saturation. The saturation deficit at each period was multiplied by the diffusion constant (k), and the product added or subtracted to the rate-of-change curve to correct for diffusion loss or gain. The corrected rate-of-change curve then showed the community metabolism which might have resulted had there been no diffusion. A diffusion constant (k) of about 1.0 gm/M<sup>3</sup>/hr. was calculated for all of the sampling stations in this study.

On the corrected rate-of-change curve, the rate of community respiration was shown by drawing a line from the dawn point to the lowest point at night (Figures 3 and 7 through 20). The amount of respiration in grams

per cubic meter per day ( $\text{gm}/\text{M}^3/\text{day}$ ) was determined by measuring the area between the respiration line and the zero rate of change line. Community respiration is indicated by the stippled area in Figure 3.

Gross community photosynthesis, including simultaneous respiration, is represented in the area indicated by plus marks between the respiration line and the daytime hump of the corrected rate-of-change curve. The amount of photosynthesis in  $\text{gm}/\text{M}^3/\text{day}$  was determined by measuring the enclosed area.

Since photosynthesis occurs on the basis of area exposed to sunlight, it is necessary to convert the community photosynthesis and respiration values to surface area. Depth of light penetration (euphotic zone), was estimated to be one meter by Secchi disc measurements. Gross community photosynthesis in  $\text{gm}/\text{M}^3/\text{day}$  was multiplied by the depth of the euphotic zone in meters to obtain the gross primary productivity ( $P_g$ ) in  $\text{gm}/\text{M}^2/\text{day}$ . Likewise, community respiration ( $R$ ) was multiplied by the depth to obtain respiration in  $\text{gm}/\text{M}^2/\text{day}$ .

#### Measurement of Day-Net Productivity

The amount of oxygen released during the daylight hours minus simultaneous community respiration may be called day-net photosynthesis. Oswald, et al. (1957) used the day-net photosynthesis to estimate the photosynthetic production of sewage-oxidation ponds. To determine day-net photosynthesis in  $\text{gm}/\text{M}^3/\text{day}$  the minimum dissolved oxygen concentration was subtracted from the maximum dissolved oxygen concentration. The day-net photosynthesis in  $\text{gm}/\text{M}^3/\text{day}$  was multiplied by the depth of the euphotic zone in meters to obtain day-net productivity in  $\text{gm}/\text{M}^2/\text{day}$  (Table V).

## CHAPTER IV

### RESULTS AND CONCLUSIONS

#### Gross Primary Productivity

No free oxygen was found in the first part of either pond series. Toxicity of the effluent may have prevented the growth of algae. At Refinery A, oxygen was first observed in Holding Pond Number 1 after about 23 days holding time and the highest primary productivity value ( $23.38 \text{ gm/M}^2/\text{day}$ ) occurred at that point (Table III and Figure 4). At Refinery B, gross primary productivity increased rapidly from a low point of  $12.28 \text{ gm/M}^2/\text{day}$  in Oil Pond Number 3 at about 16 days holding time to a peak of  $21.66 \text{ gm/M}^2/\text{day}$  in Oxidation Pond Number 2 at about 18 days holding time (Table III and Figure 5).

Gross primary productivity values progressively decreased as the water traversed each pond system (Figures 4 and 5). Linear regression analyses of gross primary productivity as a function of time in days were  $-0.59 \text{ gm/M}^2/\text{day}$  at Refinery A and  $-0.32 \text{ gm/M}^2/\text{day}$  at Refinery B.

The high values which occurred in Bay 1 of Oxidation Pond Number 4 at about 48 days holding time seem to be out of sequence (Table III and Figures 5 and 6) and may be connected with the practice of recycling about 230,000 gallons per day from this bay back to the refinery for cooling processes. It seems more logical to expect that the productivity and respiration values leveled off after the end of Oxidation Pond Number 3 at about 37 days holding time.

The changes observed in the gross primary productivity in this study may be explained by the influence of available nutrients. It may be assumed that bacterial decomposition of organic matter in the refinery effluent added an excess of carbon dioxide to the community which was used by algae in photosynthesis and caused a high gross primary productivity. The progressive decrease in productivity may be attributed to the decrease in the available carbon dioxide. Bacterial decomposition probably reduced the amount of organic material as the water moved from pond to pond and less and less carbon dioxide was available for algal photosynthesis.

Gross primary productivity ( $P_g$ ) values reached a maximum of 23.38 gm/M<sup>2</sup>/day (Table III). Odum and Hoskin (1958) reported values of 7.0 to 18.0 gm/M<sup>2</sup>/day on the grass flats of Redfish Bay, Texas, at a station affected by a treated sewage outfall. Odum (1956) estimated gross primary productivity at 60.0 gm/M<sup>2</sup>/day in the recovery zone of a polluted stream in Indiana. Odum (1956) computed 39.0 gm/M<sup>2</sup>/day for the polluted River Lark, England, from data reported by Butcher, et al. (1930). Most unpolluted quiet waters yield productivity values of smaller magnitudes. Odum and Hoskin (1958) reported midsummer values of 2.18 to 4.52 gm/M<sup>2</sup>/day in a farm pond near Durham, North Carolina, and 2.70 gm/M<sup>2</sup>/day from Baffin Bay, Riviera, Texas. Computations from data reported by Verduin (1956) in seven Wisconsin lakes yielded values of 2.85 to 10.40 gm/M<sup>2</sup>/day. These lower production values are comparable to the 7.50 gm/M<sup>2</sup>/day estimated at the last sampling station at Refinery B. As the water entered the pond system it had characteristics similar to other polluted situations and at the end of the system it was approaching an unpolluted condition.

Efficiency of the algae in converting solar radiation into carbohydrates is summarized in Table IV. Algae, in general, require about



118,000 gram-calories of solar radiation to release one mole of oxygen or 3680 gram-calories to release one gram of oxygen (Oswald, et al., 1957). The visible solar radiation was estimated from U. S. Weather Bureau data for Ft. Worth, Texas, Oklahoma City, Oklahoma, and Manhattan, Kansas (U. S. Weather Bureau, 1960). The efficiency was determined by modifying a formula used by Oswald, et al. (1957) for estimating oxygen production in sewage oxidation ponds;

$$W_{O_2} \text{ (gm } O_2/M^2/\text{day)} = F S/3680.$$

To estimate efficiency, this formula may be modified to;

$$F = \frac{(3680 W_{O_2})}{10,000 S} 100$$

where  $F$  = per cent efficiency,

$W_{O_2}$  = weight of oxygen in grams per square meter per day,

$S$  = visible solar radiation which penetrates a water surface in calories per square centimeter, and

10,000 square centimeters = one square meter.

Maximum efficiencies of 3.53 per cent at Refinery A and 3.60 per cent at Refinery B were observed at points of highest productivity (Table IV). Dorris, et al. (in press) reported efficiency values of 0.5 to 1.5 per cent in refinery effluent holding ponds in Oklahoma. Oswald, et al. (1957) reported efficiency values of about 1.0 to 8.0 per cent in shallow sewage oxidation ponds in a pilot-plant study in California. Day-net oxygen production values were used to determine the efficiency values by both authors and did not take into consideration respiration or diffusion losses. In the present study, more realistic efficiencies were estimated using gross primary productivity values.

### Community Respiration

Community respiration is composed of the combined oxygen uptake of living organisms present in the water and the decay and decomposition of the organic matter suspended in the water or settled on the bottom. In a community with a small amount of organic matter, productivity may exceed community respiration, but if there is a large amount of organic matter, community respiration may exceed productivity.

The large spring at Silver Springs, Florida, is an example of a community in which there is an excess of productivity over community respiration (Odum, 1957a). The community respiration and organic matter concentration were relatively low at the beginning of the spring system. As the water moved downstream an increase in community respiration was accompanied by an increase in the concentration of organic matter. Gross primary productivity increased downstream at a slower rate than did the community respiration, and the values approached each other at the lower end of the stream. Community respiration was not great enough to utilize all of the newly created organic matter and the excess was carried downstream and gradually increased in quantity. The concentration at any point downstream was an aggregate of the excess occurring there plus the inflow from upstream. When there is a progressive increase in organic matter concentration in a lake it is said to be undergoing eutrophication (Welch, 1952). Possibly this term might be applied to Silver Springs.

The present study reports an example in which community respiration exceeded gross primary productivity at every sampling station (Table III and Figures 4 and 5). Community respiration exceeded gross primary productivity because the respiration processes utilized more organic matter than was produced by the green plants. This higher respiratory rate was

possible because of the steady inflow of organic matter as refinery effluent.

Analysis of regression of community respiration as a function of time in days showed a progressive decrease in the rate of respiration as the water traversed each pond system (Figures 4 and 5). The regression values were  $-0.76 \text{ gm/M}^2/\text{day}$  at Refinery A and  $-0.41 \text{ gm/M}^2/\text{day}$  at Refinery B. The progressive decline in community respiration indicated a progressive reduction in the concentration of organic matter. In both series of refinery ponds community respiration approached gross primary productivity at or near the end of the system (Table III), indicating that a balance between the two processes was being attained. Community respiration values at the last sampling stations of the two pond systems in this study were  $15.72 \text{ gm/M}^2/\text{day}$  at Refinery A and  $8.52 \text{ gm/M}^2/\text{day}$  at Refinery B as compared to  $29.00$  and  $25.76 \text{ gm/M}^2/\text{day}$  respectively at the beginning (Table III). Community respiration values in most natural waters are  $1.6$  to  $8.5 \text{ gm/M}^2/\text{day}$  (Odum and Hoskin, 1958). The addition of organic substances to an aquatic community may have a permanent affect on the metabolism of the community, resulting in a higher level at which stabilization occurs.

Conclusions on community respiration were affected by the assumptions involved in the location of the respiration line on a rate-of-change curve (Figures 3 and 7 through 20). When drawing the respiration line one assumes that community respiration occurs at a uniform rate throughout the day and night. This assumption is probably not true but since it is impossible to measure respiration during the period of photosynthesis one must assume a straight line. At best the respiration line was produced arbitrarily.

### Day-Net Productivity

Oxygen productions commonly reported from sewage-oxidation ponds are actually estimates of day-net productivity. Day-net productivity is the difference between the daily maximum and minimum dissolved oxygen concentrations. Since respiration and diffusion occur simultaneously with oxygen production, day-net values do not measure the oxygen that is lost. Failure to include oxygen lost from the community leads to erroneous productivity conclusions. Productivity measurements by diurnal rate-of-change curves (Figures 7 through 20) yield a more realistic value because they include community respiration and can be corrected for diffusion.

Discussion of day-net productivity is presented here for a comparison of values obtained in this study to production in sewage-oxidation ponds. Oswald, et al. (1957) reported day-net values of 12.4 to 19.7 gm/M<sup>2</sup>/day in sewage-oxidation ponds that were 36 inches deep. Values obtained in this study were 2.60 to 9.60 gm/M<sup>2</sup>/day (Table V). It appears that sewage-oxidation ponds are higher in day-net productivity.

Day-net productivity values in both refinery-pond systems progressively decreased as the water moved from pond to pond (Figure 6). Linear regression values for the daily reduction were -0.24 gm/M<sup>2</sup>/day at Refinery A and -0.17 gm/M<sup>2</sup>/day at Refinery B. Bacterial reduction of the nutrient source probably accounts for the progressive decrease in productivity shown in Figure 6.

### Discussion

Adverse effects may occur when effluents containing high algal populations are dumped into receiving streams. If the algae continue to live, their respiratory processes may place excessive burdens upon the oxygen

content of the receiving stream. If the algae die, their decomposition will require oxygen. Either alternative may have undesirable effects on the stream biota. Since algal activity decreased as holding time increased in the effluent-holding ponds, it may be presumed that there was also a reduction in algal populations. Observations supported this hypothesis. In other words, the algal populations were reduced to the point where they would probably have little undesirable effect on the receiving stream.

## CHAPTER V

### SUMMARY

1. A study was made to estimate the primary productivity due to algal photosynthesis in the effluent-holding ponds of two oil refineries.
2. The productivity estimates were made from diurnal changes in oxygen concentrations.
3. Linear regression of gross primary productivity and community respiration on holding time showed a progressive decrease in both productivity and respiration as the water traveled from pond to pond.
4. Gross primary productivity decreased from 23.38 gm/M<sup>2</sup>/day to 14.20 gm/M<sup>2</sup>/day at Refinery A and from 21.66 gm/M<sup>2</sup>/day to 7.50 gm/M<sup>2</sup>/day at Refinery B.
5. Community respiration decreased from 29.00 gm/M<sup>2</sup>/day to 15.72 gm/M<sup>2</sup>/day at Refinery A and from 25.76 gm/M<sup>2</sup>/day to 8.52 gm/M<sup>2</sup>/day at Refinery B.
6. Community respiration exceeded gross primary productivity at every sampling station.
7. The gross primary productivity and community respiration values approached each other near the end of the pond system indicating that stabilization was being attained.
8. Efficiency of the algae to convert solar radiation to carbohydrates was estimated to be 1.0 to 3.60 per cent.

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## APPENDIX

TABLE I

THE DISSOLVED OXYGEN CONCENTRATION IN MG/LITER AND THE  
PER CENT SATURATION AT REFINERY A

Sampling date		6:00am	11:00am	1:00pm	3:00pm	5:00pm	7:00pm	6:00am
<u>Holding Pond #1</u>								
June 9, 1960	A	0.86	5.90	8.60	10.10	----	9.20	0.86
	B	0.80	5.10	9.50	10.40	----	10.40	0.80
June 19, 1960	A	1.35	4.00	6.80	7.20	8.30	8.30	1.35
	B	1.42	3.90	6.60	7.40	8.30	8.30	1.35
June 28, 1960	A	0.72	4.60	8.00	10.40	10.10	10.40	0.72
	B	0.86	5.10	7.40	10.10	9.20	10.40	0.86
July 8, 1960	A	0.00	5.10	8.60	10.70	11.70	11.30	1.70
	B	0.00	4.00	9.80	11.00	11.00	10.70	1.42
July 27, 1960	A	0.80	5.00	7.60	----	11.70	11.00	0.80
	B	0.86	4.50	8.00	----	11.70	11.00	0.86
Aug. 6, 1960	A	0.00	2.90	8.60	8.90	9.50	----	0.00
	B	0.00	3.20	7.40	7.80	9.20	7.80	0.00
Average		0.64	4.44	8.08	9.40	10.07	9.89	0.89
% saturation		5	60	105	120	130	128	11
<u>Holding Pond #2</u>								
June 9, 1960	A	0.00	3.00	4.90	5.90	----	6.40	0.00
	B	0.00	2.90	5.00	5.40	----	5.90	0.00
June 19, 1960	A	0.00	2.17	5.40	8.00	9.20	5.70	0.00
	B	0.00	2.30	4.70	----	8.60	5.60	0.00
June 28, 1960	A	0.00	5.40	6.40	6.80	8.30	6.40	0.00
	B	0.00	4.70	6.40	6.40	8.30	6.20	0.00
July 8, 1960	A	0.00	----	7.00	9.50	8.30	6.20	0.00
	B	0.00	3.48	7.20	8.30	8.00	6.60	0.00
July 27, 1960	A	0.00	1.78	5.60	----	8.00	7.00	0.00
	B	0.00	1.70	5.60	----	8.30	7.00	0.00
Aug. 6, 1960	A	0.00	4.90	9.20	10.10	9.50	4.20	0.00
	B	0.00	5.70	8.90	10.40	8.90	4.60	0.00
Average		0.00	3.46	6.36	7.84	8.54	5.98	0.00
% saturation		0	45	85	101	110	80	0
<u>Holding Pond #3</u>								
June 9, 1960	A	0.00	7.00	9.20	9.20	----	10.10	0.00
	B	0.00	6.60	9.20	10.10	----	10.40	0.00
June 19, 1960	A	1.80	3.40	6.00	6.80	7.20	7.20	1.80
	B	----	3.10	5.00	6.20	7.20	7.40	----
June 28, 1960	A	0.13	2.31	4.10	6.20	8.60	7.60	0.13
	B	0.56	2.24	4.10	5.90	8.00	7.60	0.56
July 8, 1960	A	0.24	3.28	6.00	9.20	8.00	7.40	0.32
	B	0.00	2.90	6.80	9.20	8.20	7.80	0.29
July 27, 1960	A	0.00	3.80	6.80	----	11.00	8.00	0.00
	B	0.00	4.00	6.80	----	10.70	8.60	0.00
Aug. 6, 1960	A	0.00	3.28	8.60	9.80	11.00	8.00	0.00
	B	0.00	2.65	7.20	9.50	10.10	----	0.00
Average		0.25	3.71	6.65	8.21	9.00	8.19	0.28
% saturation		3	50	85	105	115	105	3

TABLE I (Continued)

Sampling date		6:00am	11:00am	1:00pm	3:00pm	5:00pm	7:00pm	6:00am
<u>Holding Pond #4</u>								
June 9, 1960	A	1.10	4.10	5.40	6.20	----	6.80	1.10
	B	1.05	4.10	5.90	6.20	----	7.20	1.05
June 19, 1960	A	1.05	3.40	4.90	6.00	7.40	7.80	1.05
	B	1.05	3.28	4.70	7.00	7.40	7.40	1.05
June 28, 1960	A	0.32	3.20	5.30	6.20	7.60	7.20	0.32
	B	0.29	3.28	5.60	5.90	7.60	7.20	0.29
July 8, 1960	A	0.62	2.00	3.40	6.40	7.40	8.30	1.05
	B	0.32	1.78	3.28	6.00	6.60	7.80	1.42
July 27, 1960	A	0.42	3.60	6.40	----	10.10	10.10	0.42
	B	0.50	3.60	6.40	----	9.20	9.50	0.50
Aug. 6, 1960	A	0.00	3.28	6.00	7.40	6.00	4.10	0.00
	B	0.00	2.46	5.40	6.40	6.80	3.80	0.00
Average		0.56	3.17	5.22	6.37	7.61	7.27	0.69
% saturation		7	40	66	70	99	95	8
<u>Holding Pond #5</u>								
June 9, 1960	A	0.86	4.00	4.60	5.00	----	6.00	0.86
	B	0.86	3.90	4.50	5.40	----	5.70	0.86
June 19, 1960	A	2.72	5.00	7.40	9.50	11.70	10.10	2.72
	B	2.65	5.70	7.60	8.90	11.70	----	2.65
June 28, 1960	A	0.29	2.24	3.09	4.60	6.00	5.40	0.29
	B	0.29	2.31	3.28	4.90	6.00	5.40	0.29
July 27, 1960	A	1.05	3.80	7.60	----	10.40	11.70	1.05
	B	1.10	4.20	7.40	----	10.10	11.70	1.10
Aug. 6, 1960	A	0.00	3.00	4.20	6.20	6.20	6.20	0.00
	B	0.00	3.20	4.70	6.40	7.40	5.00	0.00
Average		0.98	3.74	5.44	6.36	8.69	7.47	0.98
% saturation		13	48	70	82	113	97	13
<u>Holding Pond #6</u>								
June 9, 1960	A	6.00	7.60	10.70	11.30	----	11.30	6.00
	B	6.00	7.60	9.20	11.00	----	10.70	6.00
June 19, 1960	A	5.10	----	9.50	9.50	9.50	----	5.10
	B	5.10	----	9.50	9.50	10.10	9.50	5.10
July 27, 1960	A	4.70	4.70	8.00	----	8.00	9.80	4.70
	B	5.10	4.40	7.80	----	8.30	9.80	5.10
Aug. 6, 1960	A	5.60	7.00	9.20	10.40	11.70	9.80	4.70
	B	5.30	7.40	9.20	10.10	11.30	10.70	4.50
Average		5.36	6.45	9.14	10.30	9.82	10.23	5.15
% saturation		65	85	120	135	126	132	67

---- indicates missing data

TABLE II

THE DISSOLVED OXYGEN CONCENTRATION IN MG/LITER AND THE  
PER CENT SATURATION AT REFINERY B

Sampling date		6:00am	11:00am	1:00pm	3:00pm	5:00pm	7:00pm	6:00am
<u>Oil Pond 3</u>								
July 12, 1960	A	3.40	6.60	7.40	8.90	9.50	8.00	3.40
	B	3.20	6.60	7.80	8.60	8.90	8.90	3.20
Aug. 22, 1960	A	0.00	4.40	6.40	5.60	8.00	4.10	0.00
	B	0.00	----	6.40	5.70	7.80	4.70	0.00
Average		1.65	5.87	7.00	7.20	8.55	6.43	1.65
% saturation		20	76	90	93	112	83	20
<u>Oxidation Pond 2</u>								
June 22, 1960	A	1.10	6.00	7.20	10.40	9.20	9.50	1.10
	B	1.00	5.40	6.80	9.80	9.50	9.20	1.00
July 12, 1960	A	2.90	6.40	7.80	9.50	9.80	9.20	2.90
	B	3.50	6.40	7.80	9.50	9.50	10.40	3.50
Aug. 22, 1960	A	0.00	8.60	13.20	12.80	10.40	11.70	0.00
	B	0.00	8.00	12.40	12.80	9.20	11.70	0.00
Average		1.42	6.80	9.20	10.80	9.60	10.28	1.42
% saturation		18	88	120	145	125	135	18
<u>Oxidation Pond 3; Bay 1</u>								
June 22, 1960	A	0.40	6.40	9.50	10.40	10.70	11.00	0.40
	B	0.30	5.90	9.20	10.40	10.70	11.00	0.30
July 12, 1960	A	----	6.80	7.60	9.80	8.30	----	----
	B	----	8.00	----	9.20	8.60	7.40	----
Aug. 22, 1960	A	0.00	3.90	7.40	8.00	----	8.30	0.00
	B	0.00	3.90	7.20	8.00	9.20	7.40	0.00
Average		0.18	5.82	8.18	9.30	9.50	9.02	0.18
% saturation		2	75	106	120	125	118	2
<u>Oxidation Pond 3; Bay 2</u>								
June 22, 1960	A	----	4.00	5.60	9.20	9.50	7.20	----
	B	4.20	3.40	5.60	----	8.90	7.60	4.20
July 12, 1960	A	4.70	6.00	----	7.20	9.20	7.40	4.70
	B	4.40	5.40	7.00	7.00	8.60	6.60	4.40
Aug. 22, 1960	A	1.80	5.60	7.40	8.60	8.60	7.60	1.60
	B	1.80	5.10	6.40	7.60	8.30	7.40	1.50
Average		3.38	4.92	6.40	7.92	8.85	7.30	3.28
% saturation		44	64	83	103	116	95	42
<u>Oxidation Pond 3; Bay 3</u>								
June 22, 1960	A	1.70	----	11.00	11.00	11.00	11.00	1.70
	B	1.50	8.30	9.50	9.80	10.10	10.70	1.50
July 12, 1960	A	4.10	5.10	5.30	5.60	6.00	6.00	4.10
	B	4.00	5.90	5.60	----	----	5.90	4.00
Aug. 22, 1960	A	0.00	2.00	4.20	5.60	6.40	4.50	1.40
	B	0.00	2.00	3.80	5.40	6.60	4.70	1.40
Average		1.88	4.66	6.57	7.48	8.02	7.13	2.35
% saturation		24	60	85	98	105	92	30

TABLE II (Continued)

Sampling date		6:00am	11:00am	1:00pm	3:00pm	5:00pm	7:00pm	6:00am
<u>Oxidation Pond 3; Bay 4</u>								
June 22, 1960	A	5.90	4.20	5.60	7.00	8.60	6.00	5.90
	B	4.90	4.10	5.40	7.00	9.20	6.00	4.90
July 12, 1960	A	3.50	4.20	4.60	5.70	5.40	3.50	3.50
	B	3.50	3.90	4.20	5.30	4.50	4.10	3.50
Aug. 22, 1960	A	0.00	2.90	4.00	4.50	3.90	4.50	0.00
	B	0.00	2.80	3.50	4.00	3.90	4.50	0.00
Average		2.97	3.68	4.55	5.58	5.92	4.77	2.97
% saturation		40	48	60	73	77	63	40
<u>Oxidation Pond 4; Bay 1</u>								
June 22, 1960	A	0.13	6.80	7.80	----	10.20	9.20	0.13
	B	0.13	6.60	8.00	8.90	9.00	9.80	0.13
Aug. 22, 1960	A	5.60	8.30	10.10	9.80	9.50	10.40	5.30
	B	6.00	8.30	10.10	9.80	10.40	10.10	5.90
Average		2.97	7.50	9.00	9.50	9.78	9.88	2.87
% saturation		40	98	117	124	128	130	37
<u>Oxidation Pond 4; Bay 3</u>								
June 22, 1960	A	2.72	2.65	5.10	6.00	6.00	5.90	2.72
	B	----	2.46	5.00	5.90	6.00	----	----
Aug. 22, 1960	A	7.40	10.10	9.80	10.70	10.40	10.40	8.00
	B	8.00	9.50	9.50	10.10	10.40	9.50	7.00
Average		6.04	6.18	7.35	8.18	8.20	8.60	5.91
% saturation		78	80	96	107	107	112	76

---- indicates missing data

TABLE III

SUMMARY OF THE COMMUNITY METABOLISM DETERMINED FROM DIURNAL RATE  
OF CHANGE CURVES (FIGURES 7 TO 20). THE GROSS PRIMARY  
PRODUCTIVITY ( $P_g$ ) AND COMMUNITY RESPIRATION  
(R) VALUES ARE IN GM/M<sup>2</sup>/DAY.

Station	$P_g$	R	Calculated Days Holding Time
Refinery A			
Pond 1	23.38	29.00	21.4
Pond 2	15.94	26.78	23.5
Pond 3	19.78	30.20	26.2
Pond 4	16.46	27.42	30.4
Pond 5	15.90	26.18	33.5
Pond 6	14.20	15.72	37.0
Refinery B			
Oil Pond 3	12.88	21.60	16.4
Oxidation Pond 2	21.66	25.76	17.9
Oxidation Pond 3			
Bay 1	19.92	26.88	20.0
Bay 2	10.44	17.62	26.0
Bay 3	11.24	19.12	31.0
Bay 4	6.00	16.42	37.0
Oxidation Pond 3			
Bay 1	15.08	17.36	48.0
Bay 3	7.50	8.52	60.4



TABLE IV  
THE PER CENT EFFICIENCY OF THE ABILITY OF ALGAE IN OIL  
REFINERY PONDS TO CONVERT VISIBLE SOLAR  
RADIATION INTO CARBOHYDRATES

Station	Gross Productivity GM/M <sup>2</sup> /Day	Per Cent Efficiency (F)
Refinery A		
Pond 1	23.38	3.53
Pond 2	15.94	2.41
Pond 3	19.78	2.99
Pond 4	16.46	2.49
Pond 5	15.90	2.40
Pond 6	14.20	2.14
Average		2.66
Refinery B		
Oil Pond 3	12.28	2.04
Oxidation Pond 2	21.66	3.60
Oxidation Pond 3		
Bay 1	19.92	3.31
Bay 2	10.44	1.73
Bay 3	11.24	1.87
Bay 4	6.00	1.00
Oxidation Pond 4		
Bay 1	15.08	2.50
Bay 2	7.50	1.24
Average		2.16

Estimated solar radiation:

Refinery A:

Total radiation = 653 gram-calories per square centimeter.

Visible radiation = 243 gram-calories per square centimeter.

Refinery B:

Total radiation = 594 gram-calories per square centimeter.

Visible radiation = 221 gram-calories per square centimeter.

TABLE V  
DAY-NET PRODUCTIVITY AS CALCULATED FROM DAILY MAXIMUM  
AND MINIMUM OXYGEN CONCENTRATIONS

Sampling Stations	Calculated Days Holding Time	Maximum Mg/L	Minimum Mg/L	Productivity GM/M <sup>2</sup> /Day*
Refinery A				
Holding Pond #1	21.4	10.07	0.64	9.43
Holding Pond #2	23.5	8.54	0.00	8.54
Holding Pond #3	26.2	9.00	0.25	8.75
Holding Pond #4	30.4	7.61	0.56	7.05
Holding Pond #5	33.5	8.69	0.98	7.71
Holding Pond #6	37.0	10.30	5.36	4.94
Refinery B				
Oil Pond #3	16.4	8.55	1.65	6.90
Oxidation Pond #2	17.9	10.80	1.42	9.38
Oxidation Pond #3				
Bay 1	20.0	9.50	0.18	9.32
Bay 2	26.0	8.85	3.38	5.47
Bay 3	31.0	8.02	1.88	6.14
Bay 4	37.0	5.92	2.97	2.95
Oxidation Pond #4				
Bay 1	48.0	9.88	2.97	6.91
Bay 3	60.4	8.60	6.04	2.56

\*Euphotic zone (depth of light penetration) estimated at one meter at all stations.



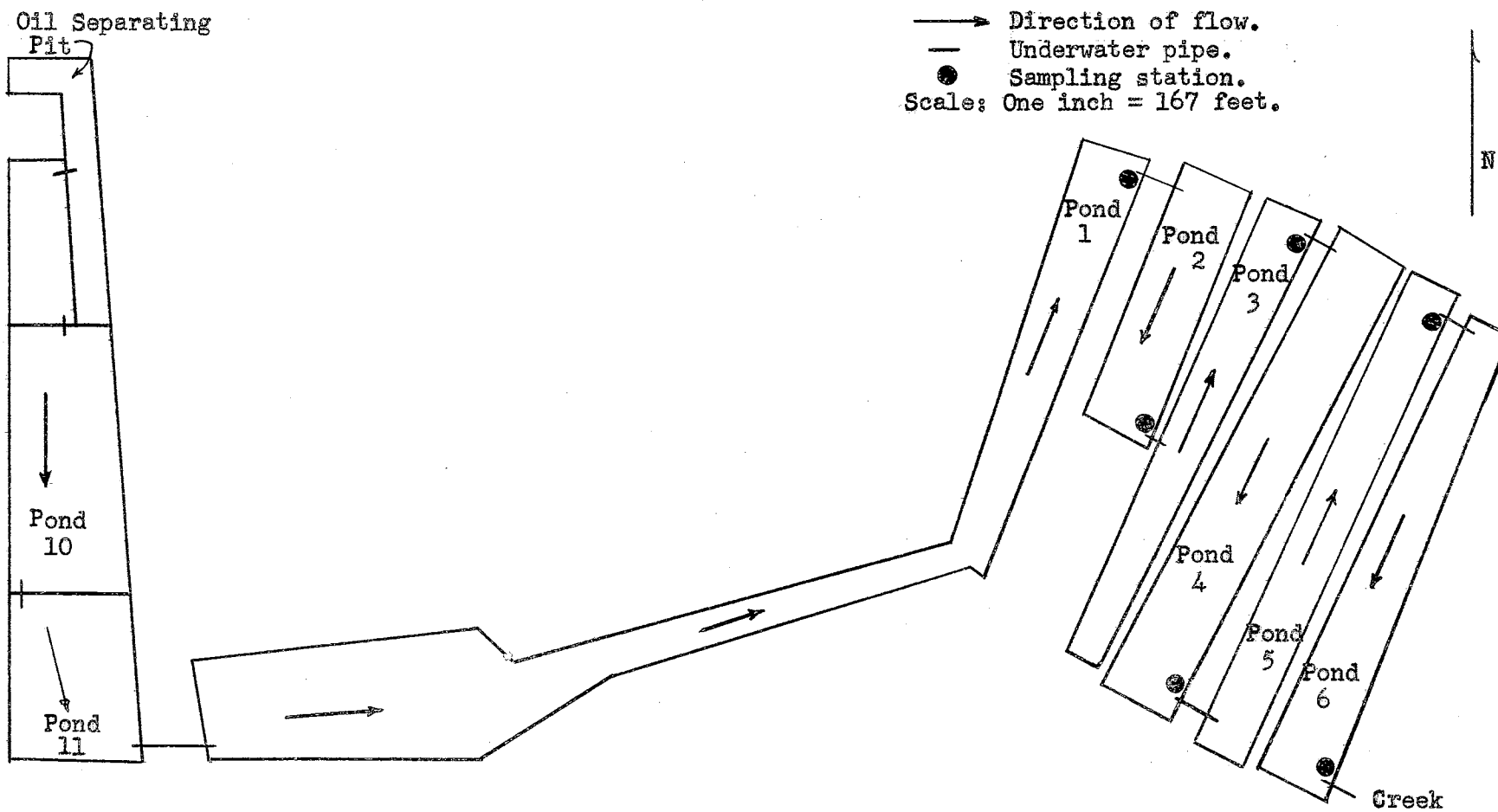


Figure 1: A diagram of the effluent-holding ponds and sampling locations at Refinery A.

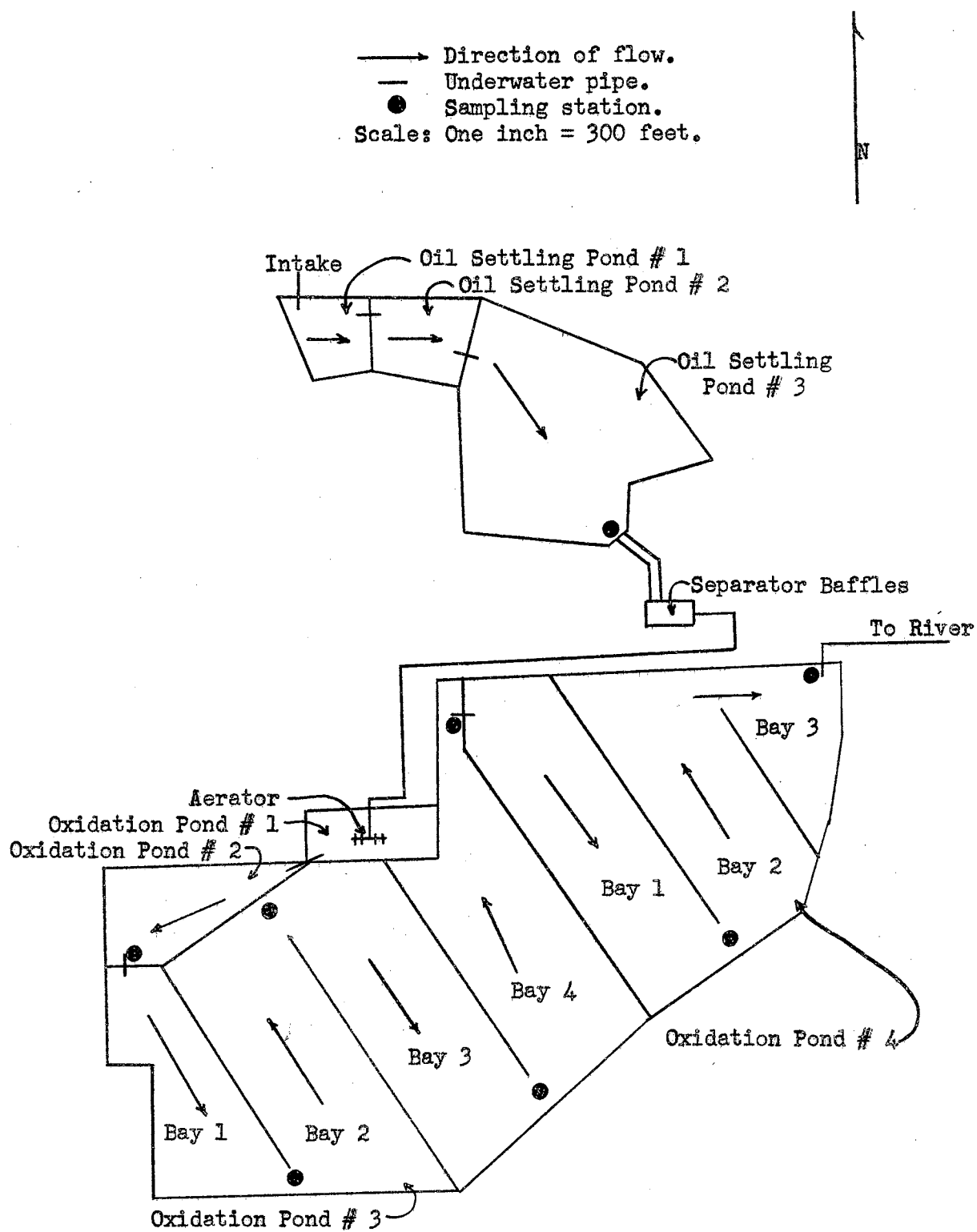
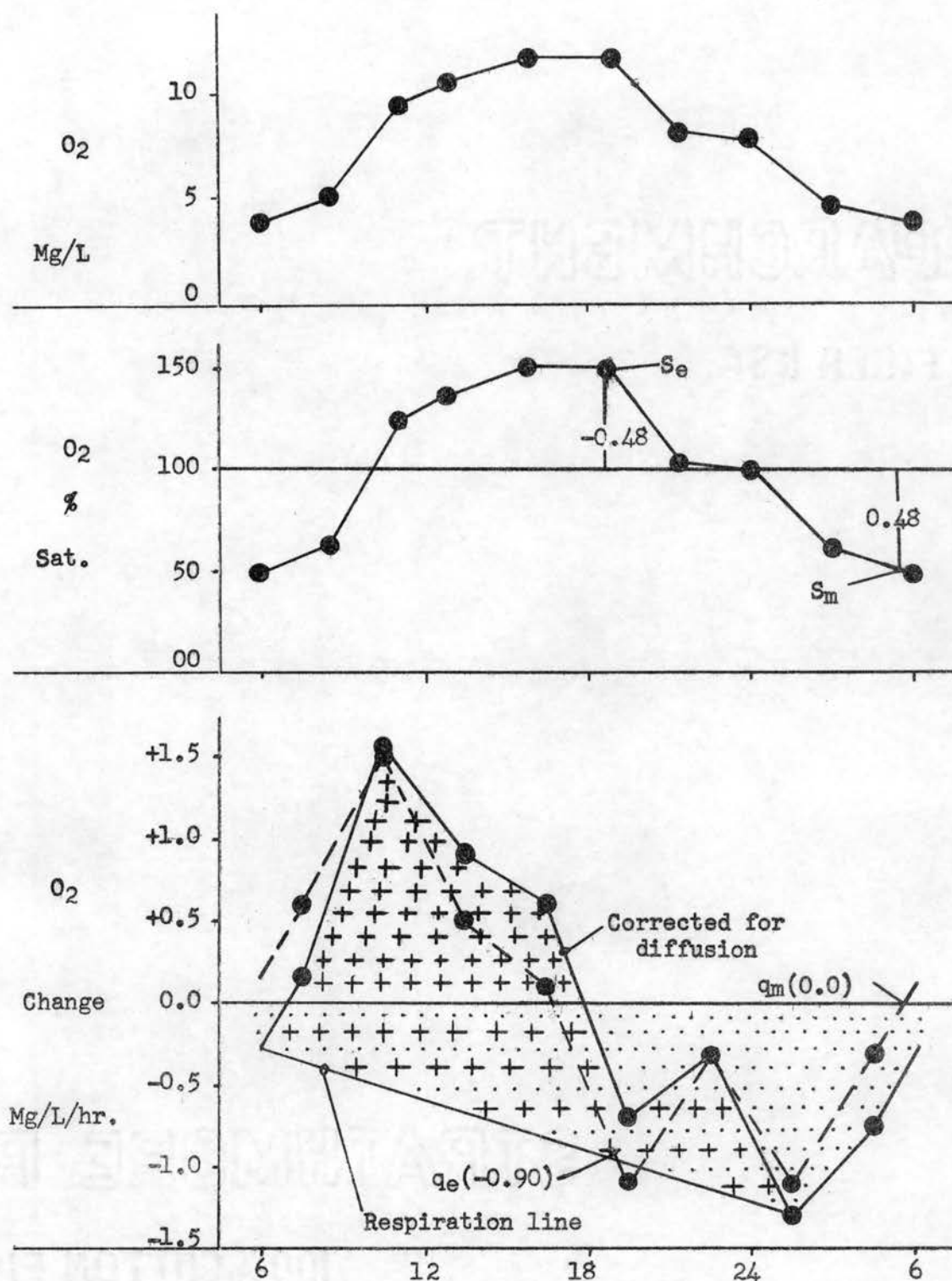


Figure 2: A diagram of the effluent-holding ponds and sampling locations at Refinery B.



$$k = \frac{q_m - q_e}{S_m - S_e} = \frac{0.0 - (-0.90)}{0.48 - (-0.48)} = \frac{0.90}{0.96} = 1 \text{ Gram/M}^3/\text{hr. at } 0\% \text{ saturation.}$$

$$R = 3.19 \text{ sq. in.} \times 6 \text{ gm/M}^3/\text{sq. in.} = 19.14 \text{ gm/M}^3/\text{day.}$$

$$P_g = 3.28 \text{ sq. in.} \times 6 \text{ gm/M}^3/\text{sq. in.} = 19.68 \text{ gm/M}^3/\text{day.}$$

Figure 3: A typical diurnal curve and calculation for gross primary productivity ( $P_g$ ), community respiration ( $R$ ), and diffusion constant ( $k$ ).

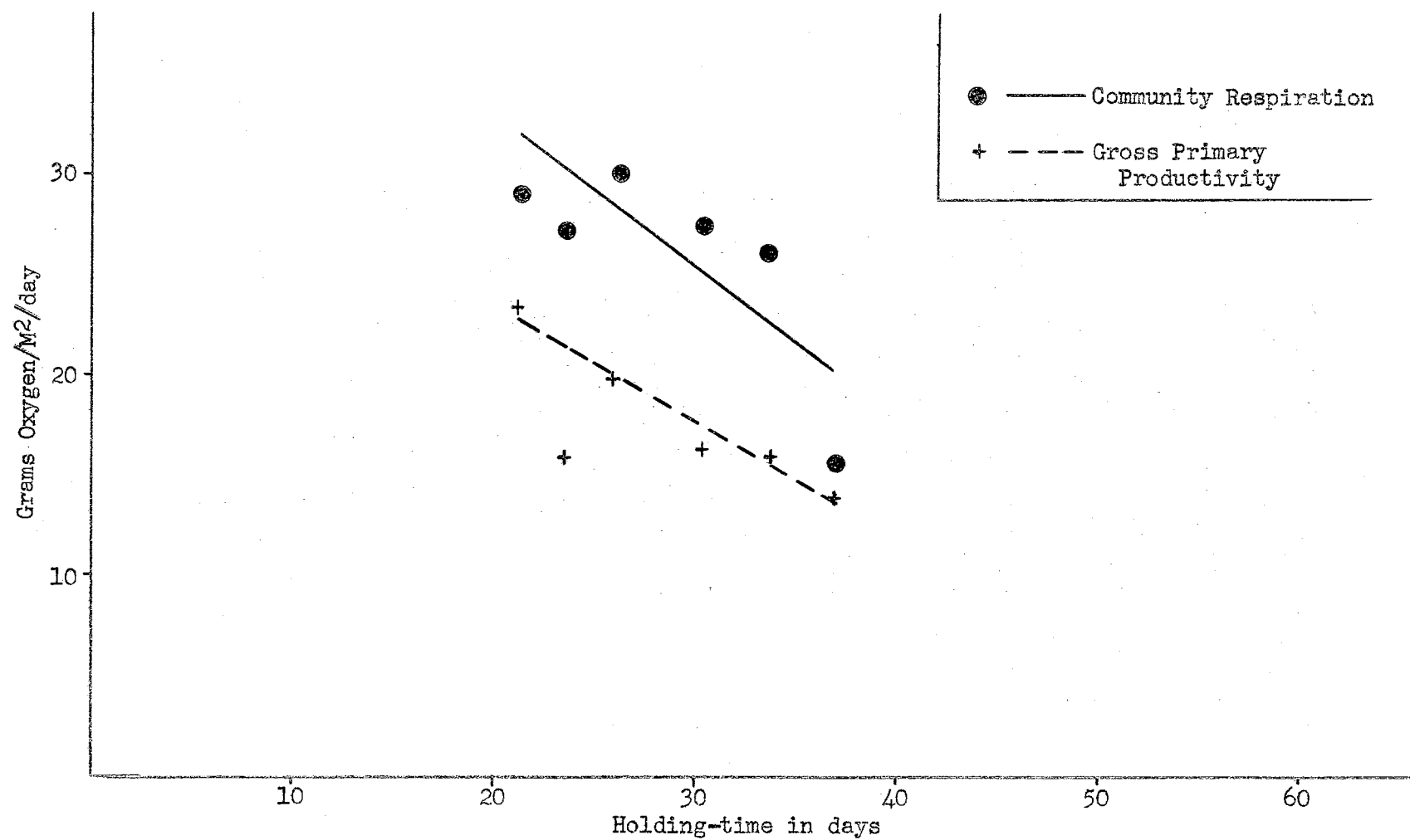


Figure 4: Regression of community respiration (R) and gross primary productivity (P<sub>g</sub>) at Refinery A.

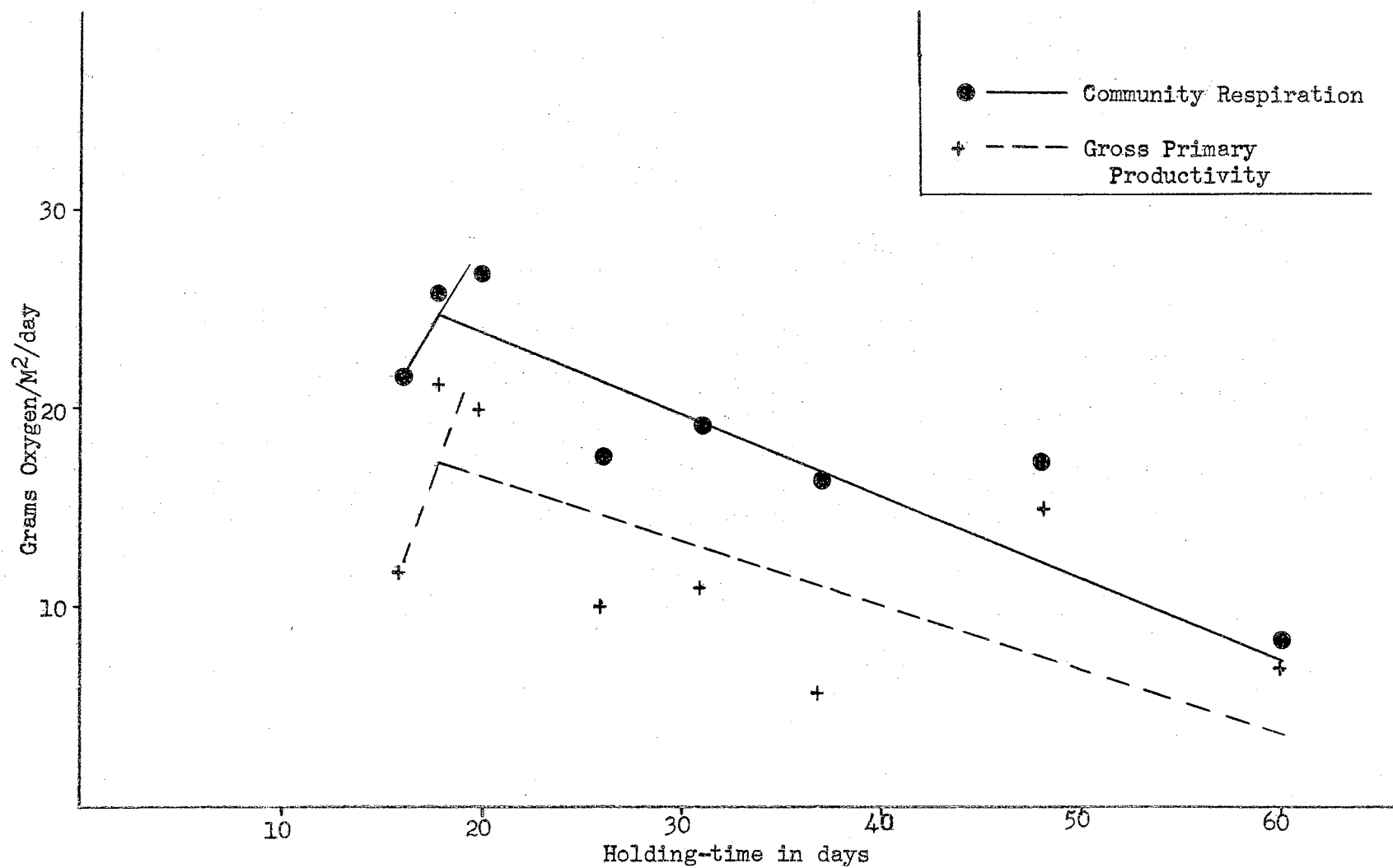


Figure 5: Regression of community respiration (R) and gross primary productivity (P<sub>g</sub>) at Refinery B.

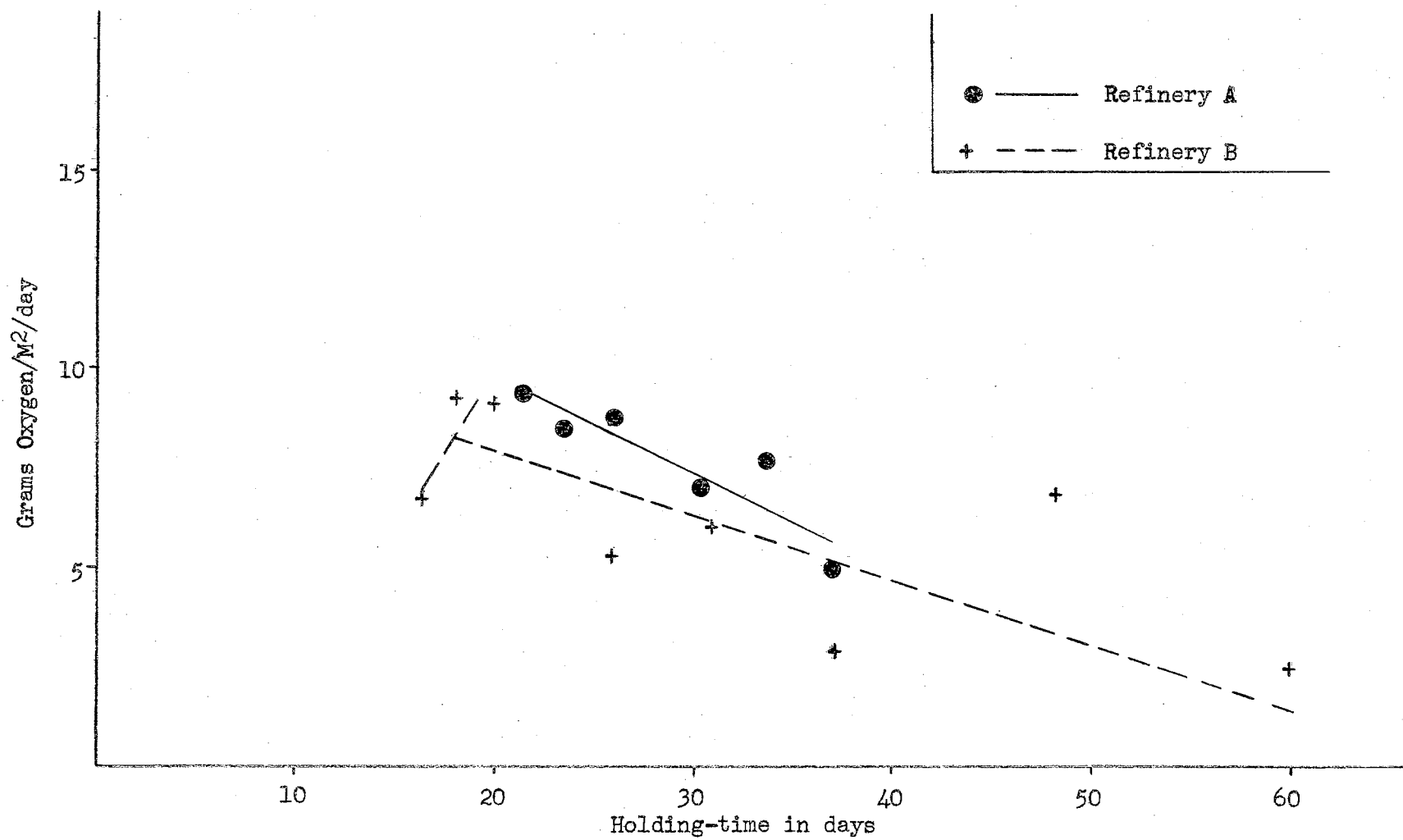


Figure 6: Regression of day-net productivity for Refinery A and B.

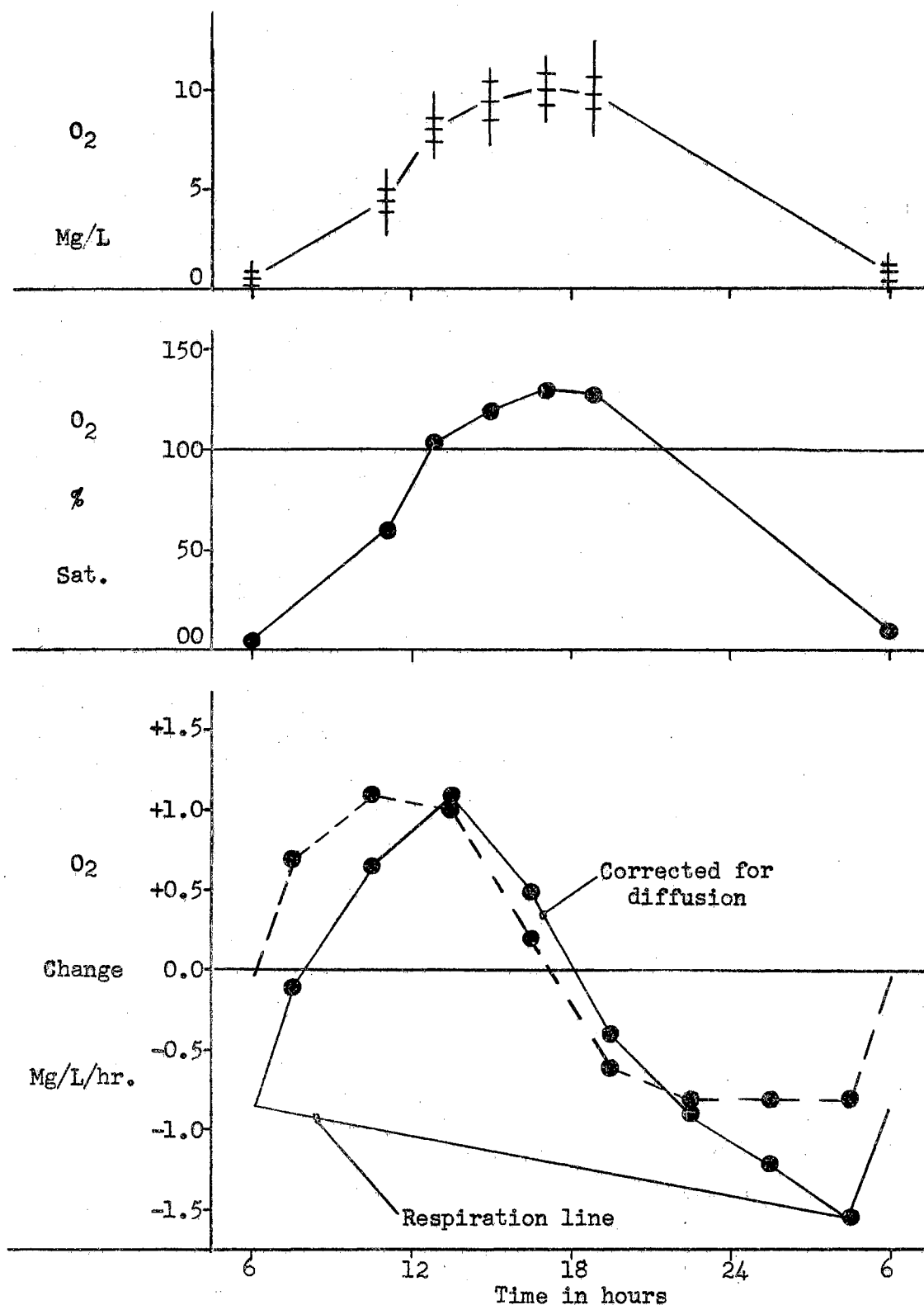


Figure 7: Diurnal oxygen curve for Holding Pond #1 (21.4 days holding time) at Refinery A. In the uppermost curve, the vertical lines indicate the range, the middle horizontal marks indicate the mean, and the outermost horizontal marks indicate the standard deviation.

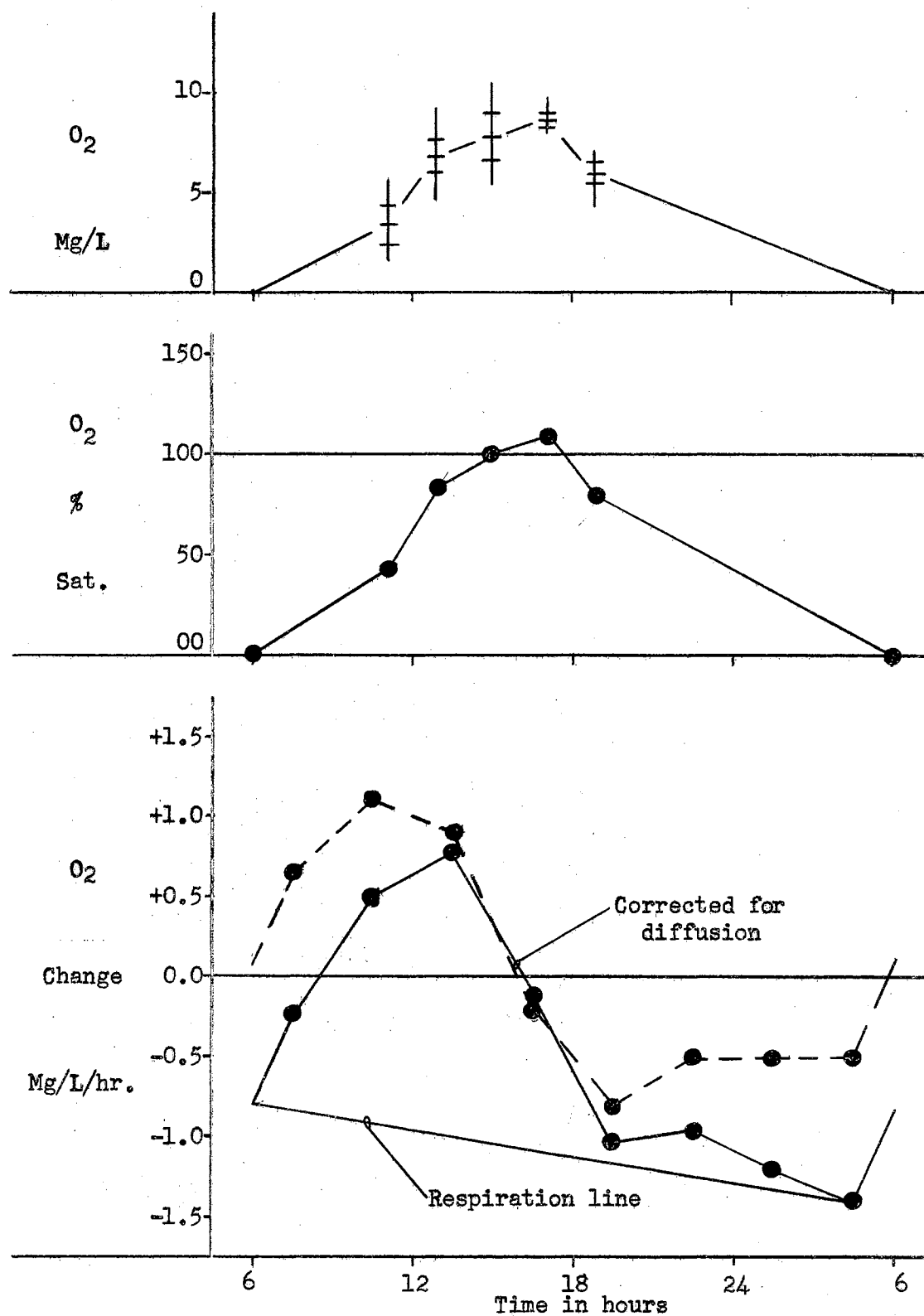


Figure 8: Diurnal oxygen curve for Holding Pond #2 (23.5 days holding time) at Refinery A. See Figure 7 for explanation of the uppermost curve.



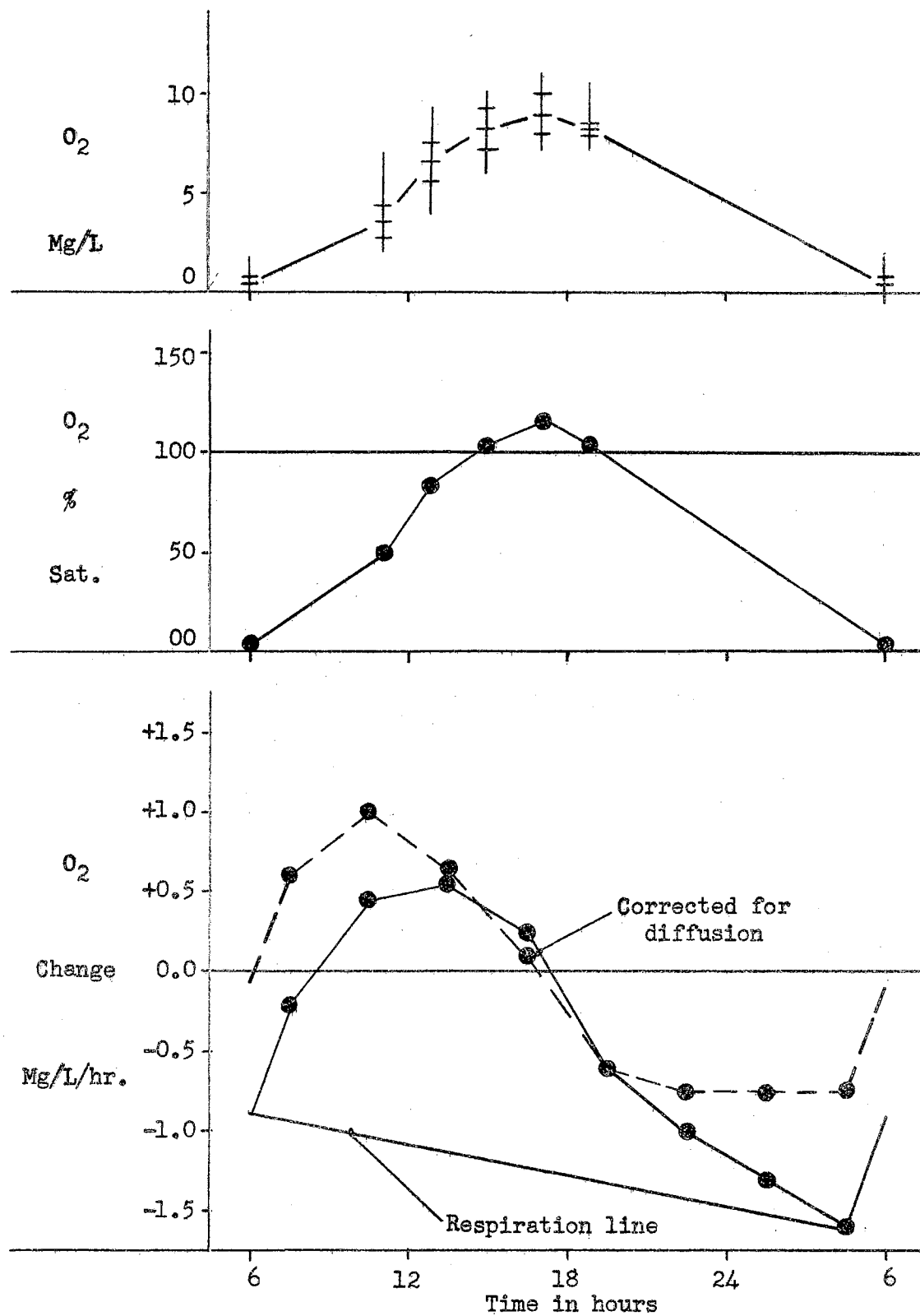


Figure 9: Diurnal oxygen curve for Holding Pond #3 (26.2 days holding time) at Refinery A. See Figure 7 for the explanation of the uppermost curve.

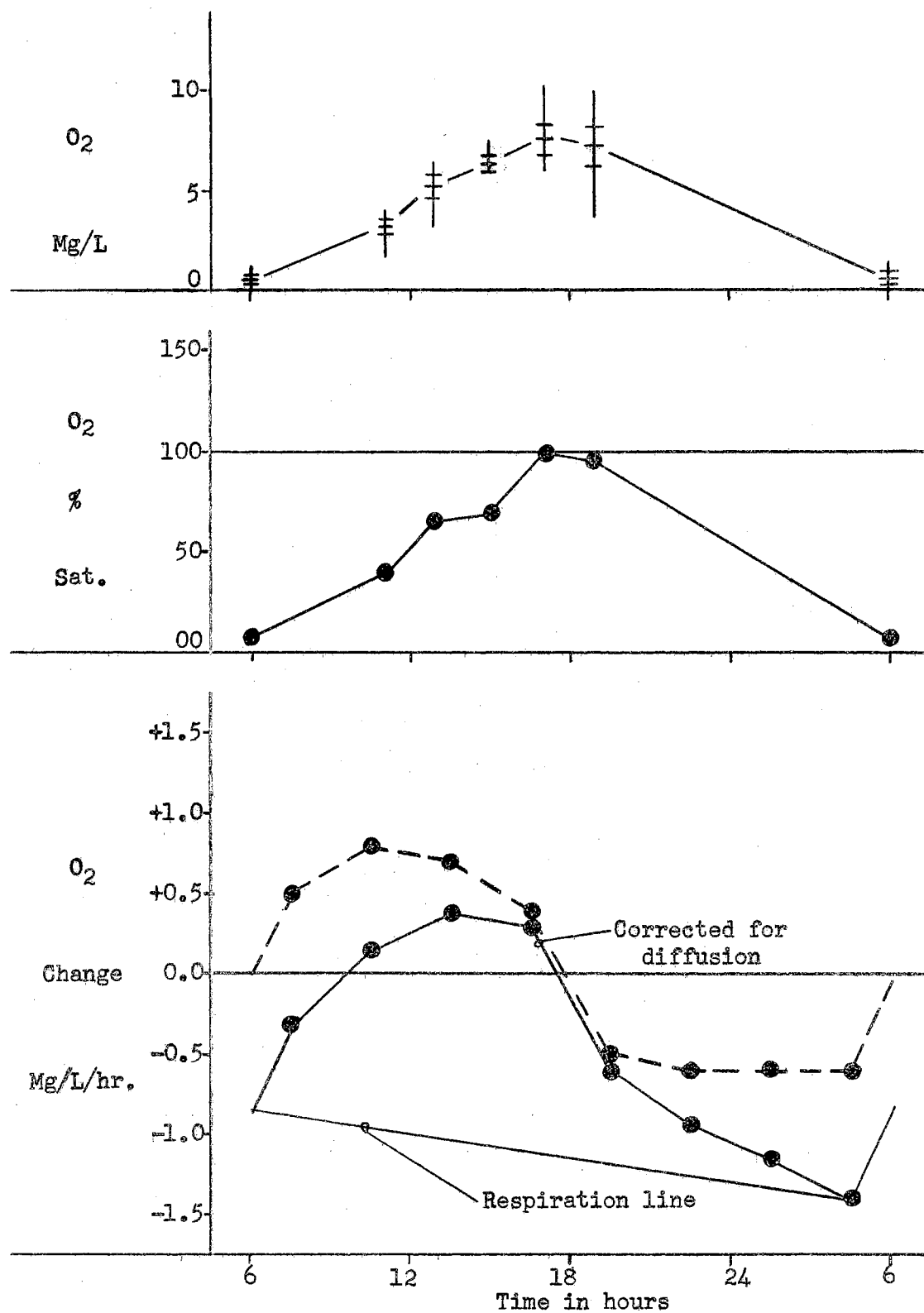


Figure 10: Diurnal oxygen curve for Holding Pond #4 (30.4 days holding time) at Refinery A. See Figure 7 for the explanation of the upper-most curve.

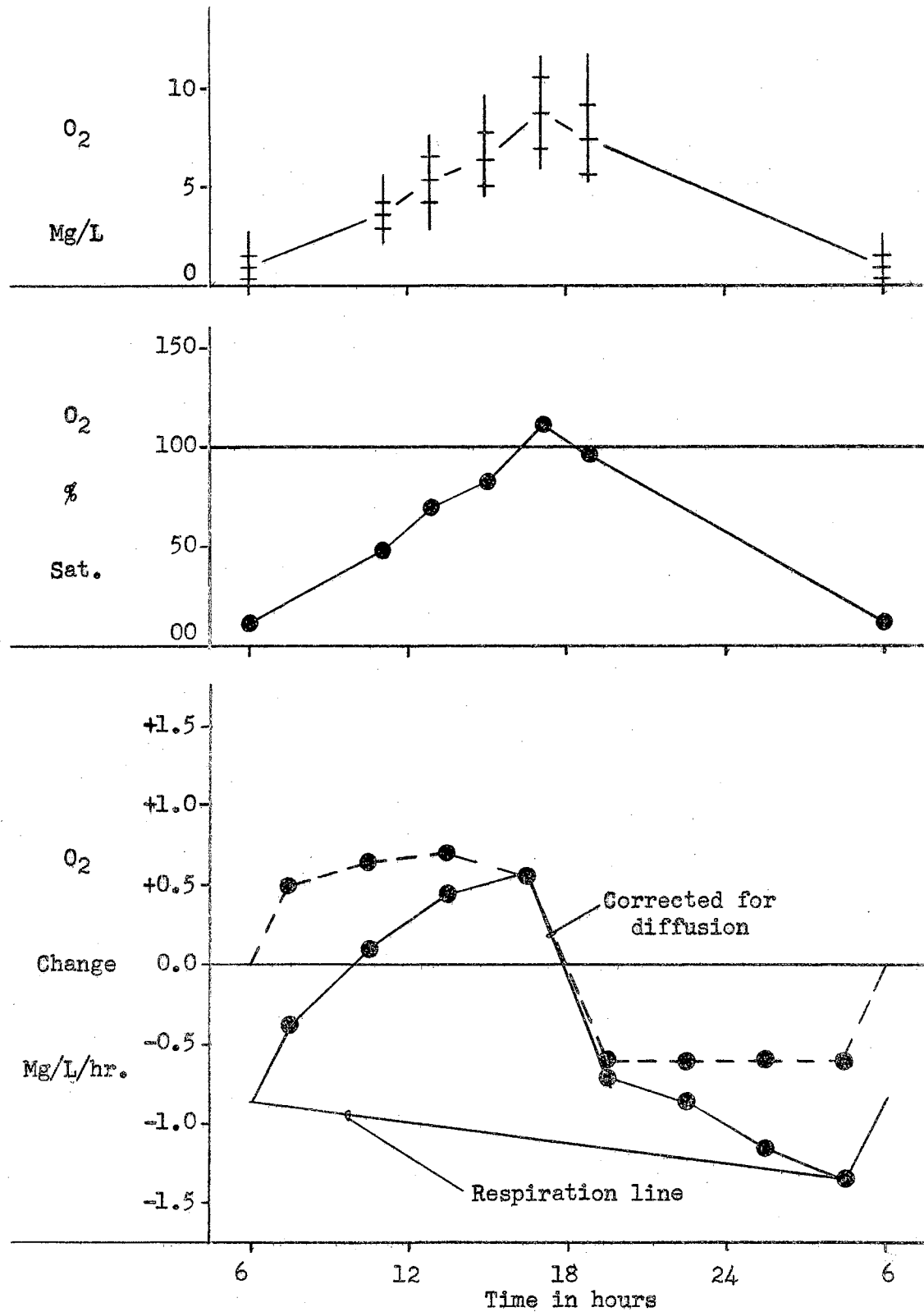


Figure 11: Diurnal oxygen curve for Holding Pond #5 (33.5 days holding time) at Refinery A. See Figure 7 for the explanation of the uppermost curve.

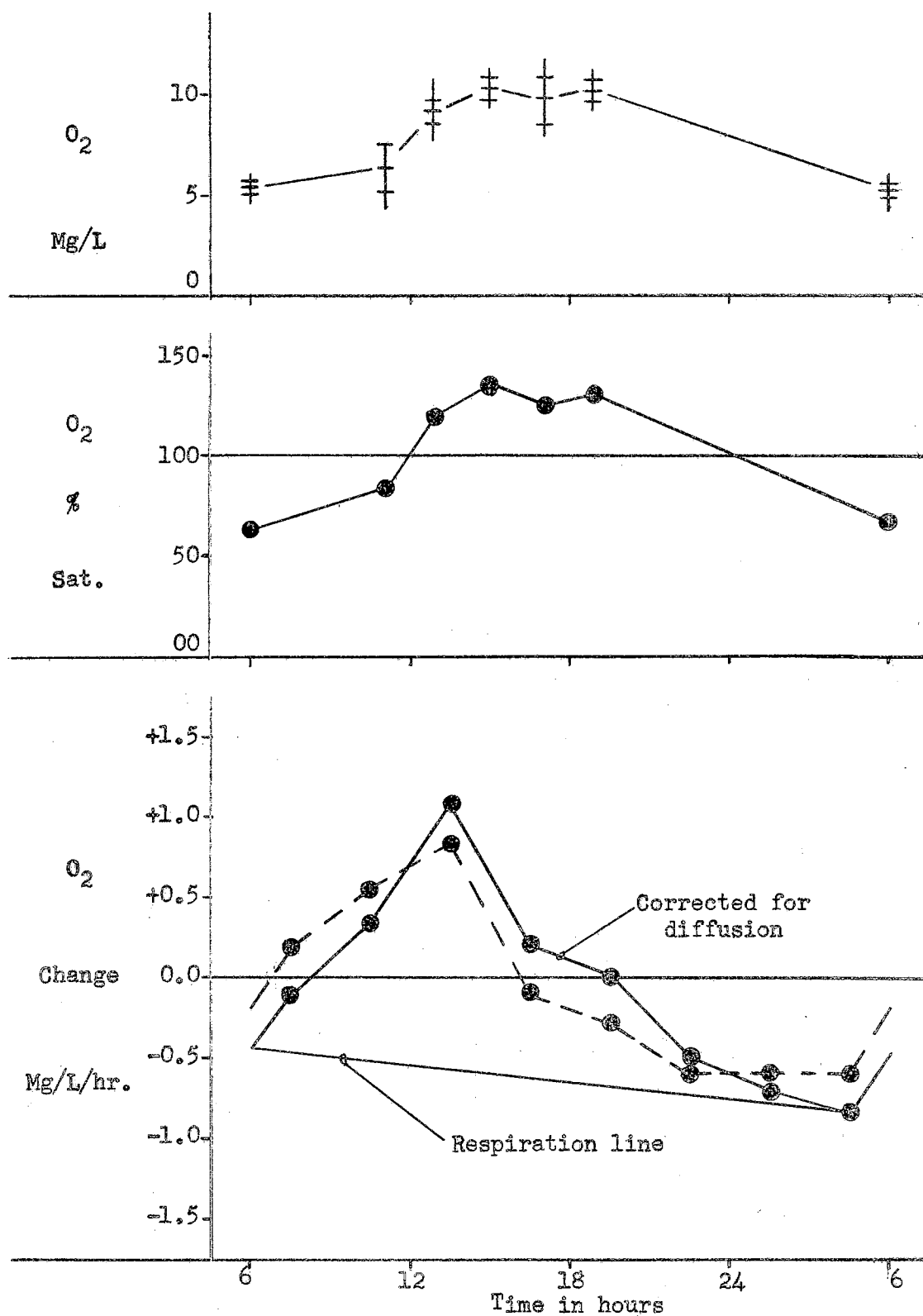


Figure 12: Diurnal oxygen curve for Holding Pond #6 (37.0 days holding time) at Refinery A. See Figure 7 for the explanation of the uppermost curve.

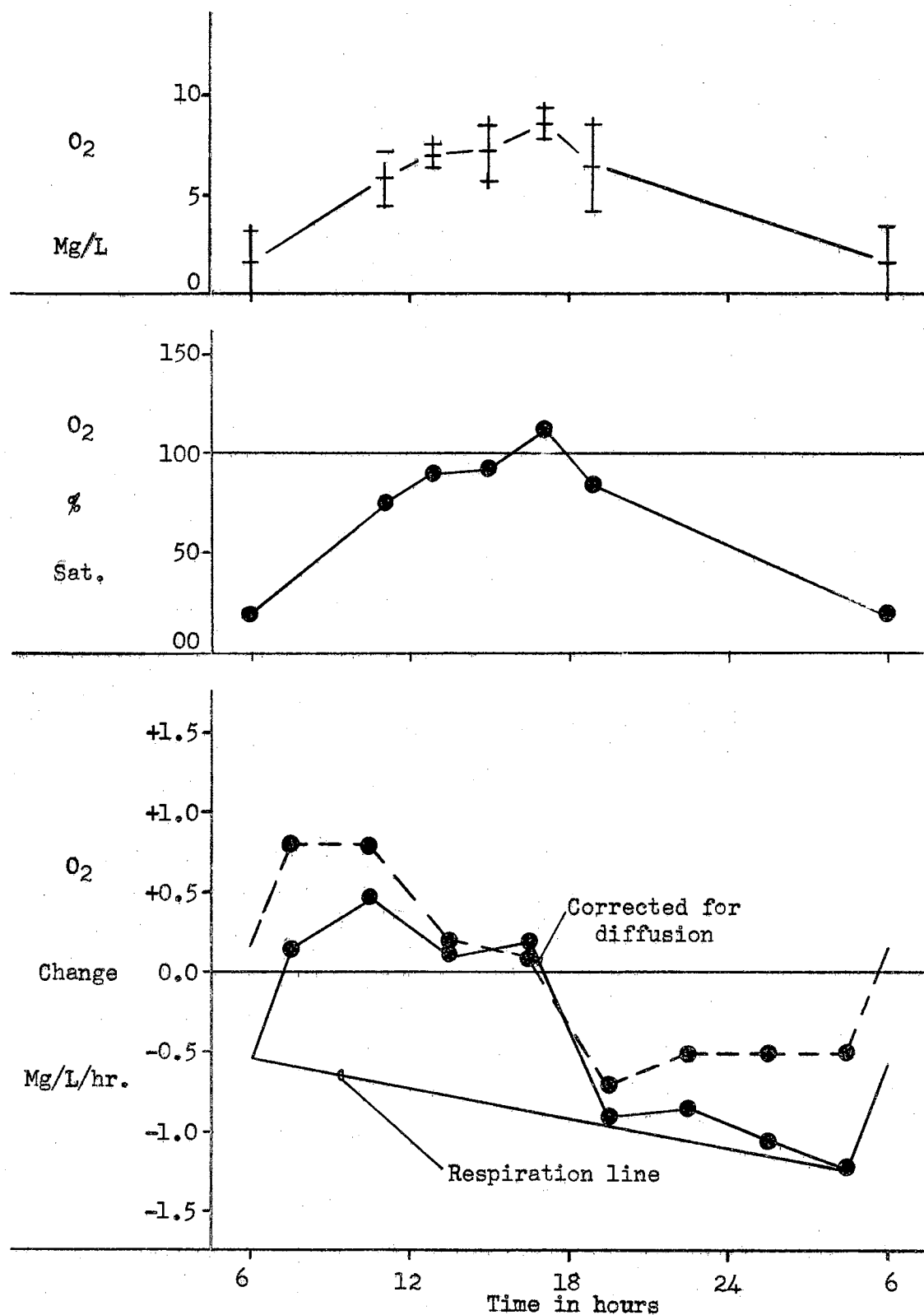


Figure 13: Diurnal oxygen curve for Oil Pond #3 (16.4 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.

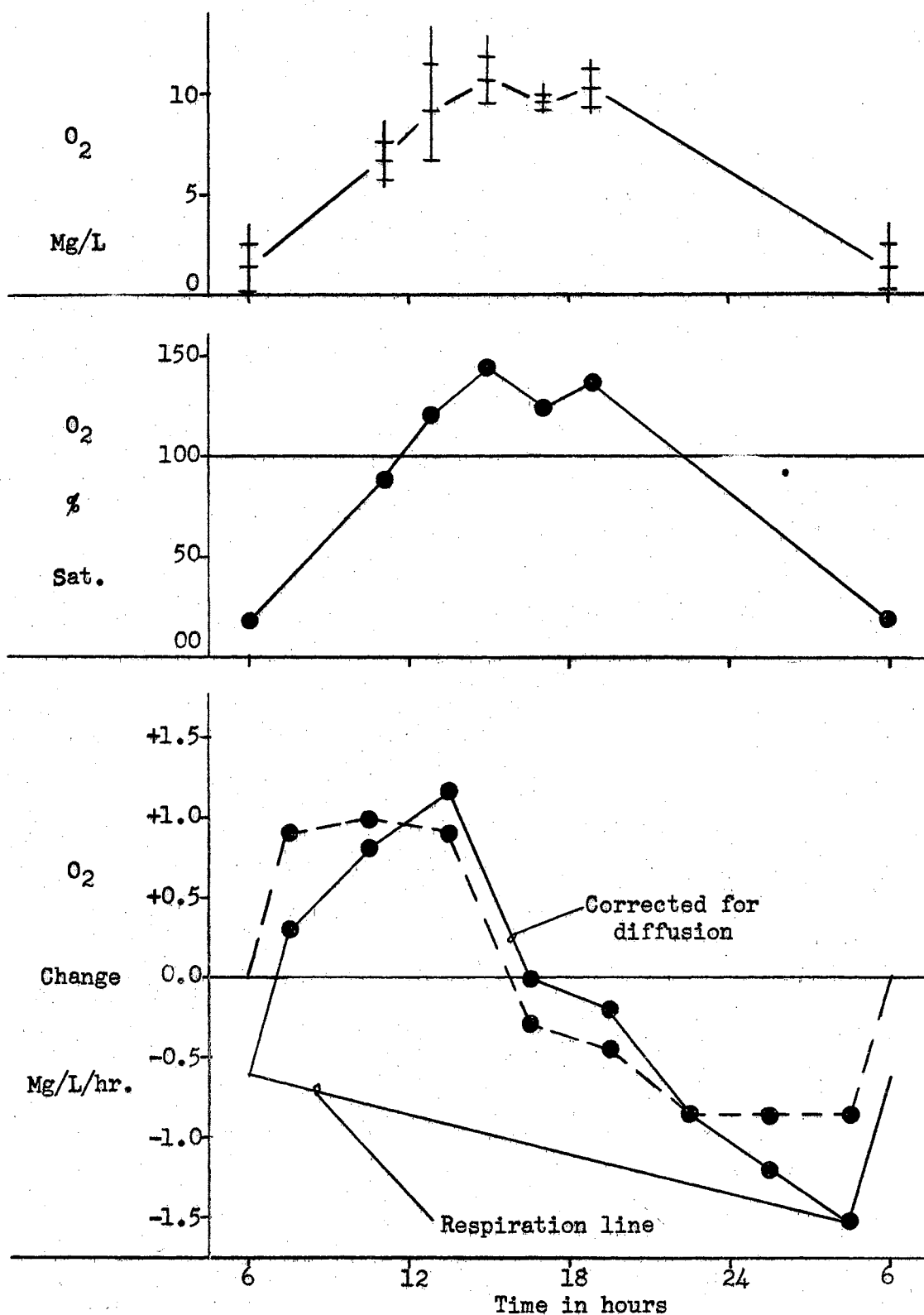


Figure 14: Diurnal oxygen curve for Oxidation Pond #2 (17.9 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.

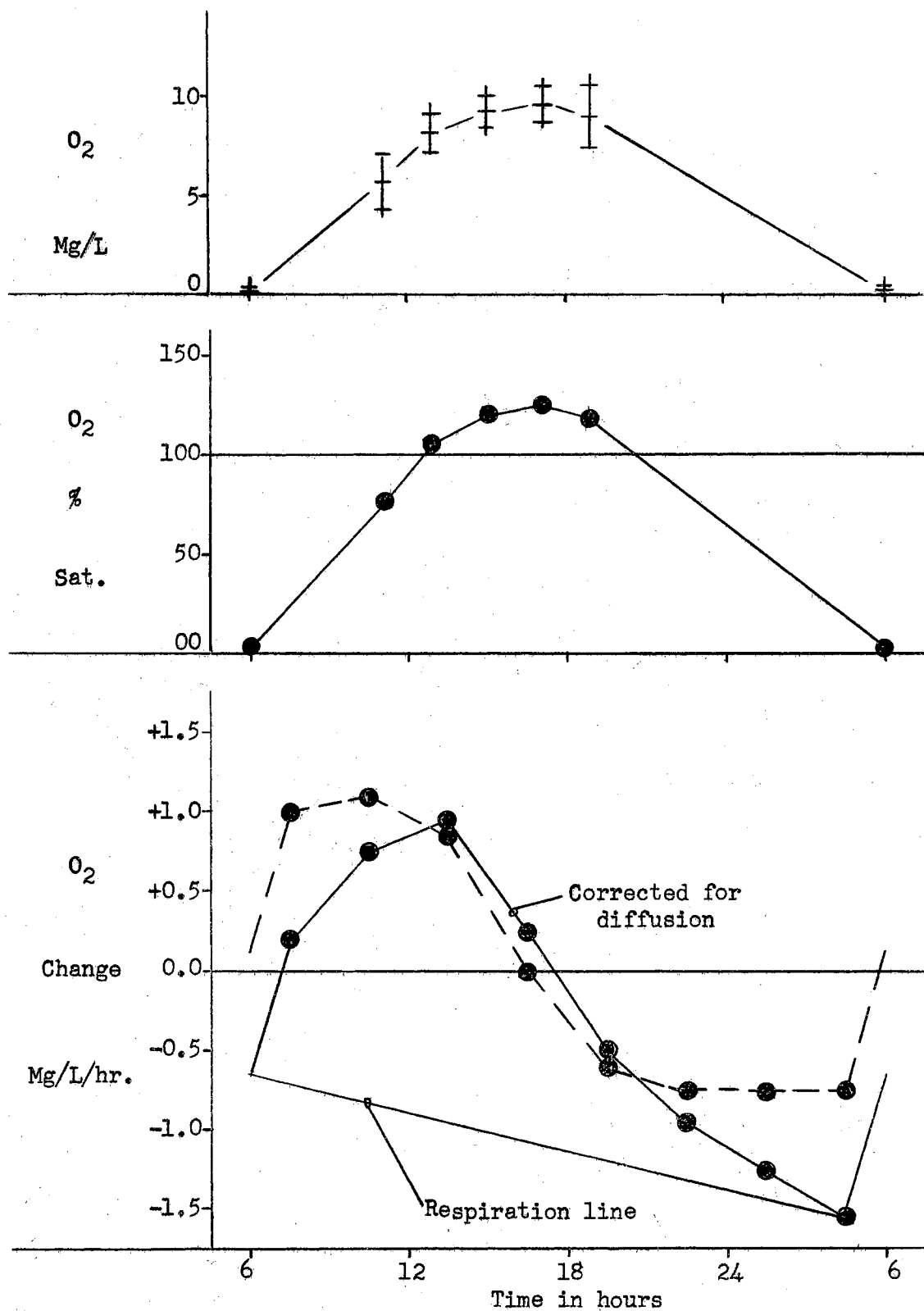


Figure 15: Diurnal oxygen curve for Bay 1 of Oxidation Pond #3 (20.0 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.

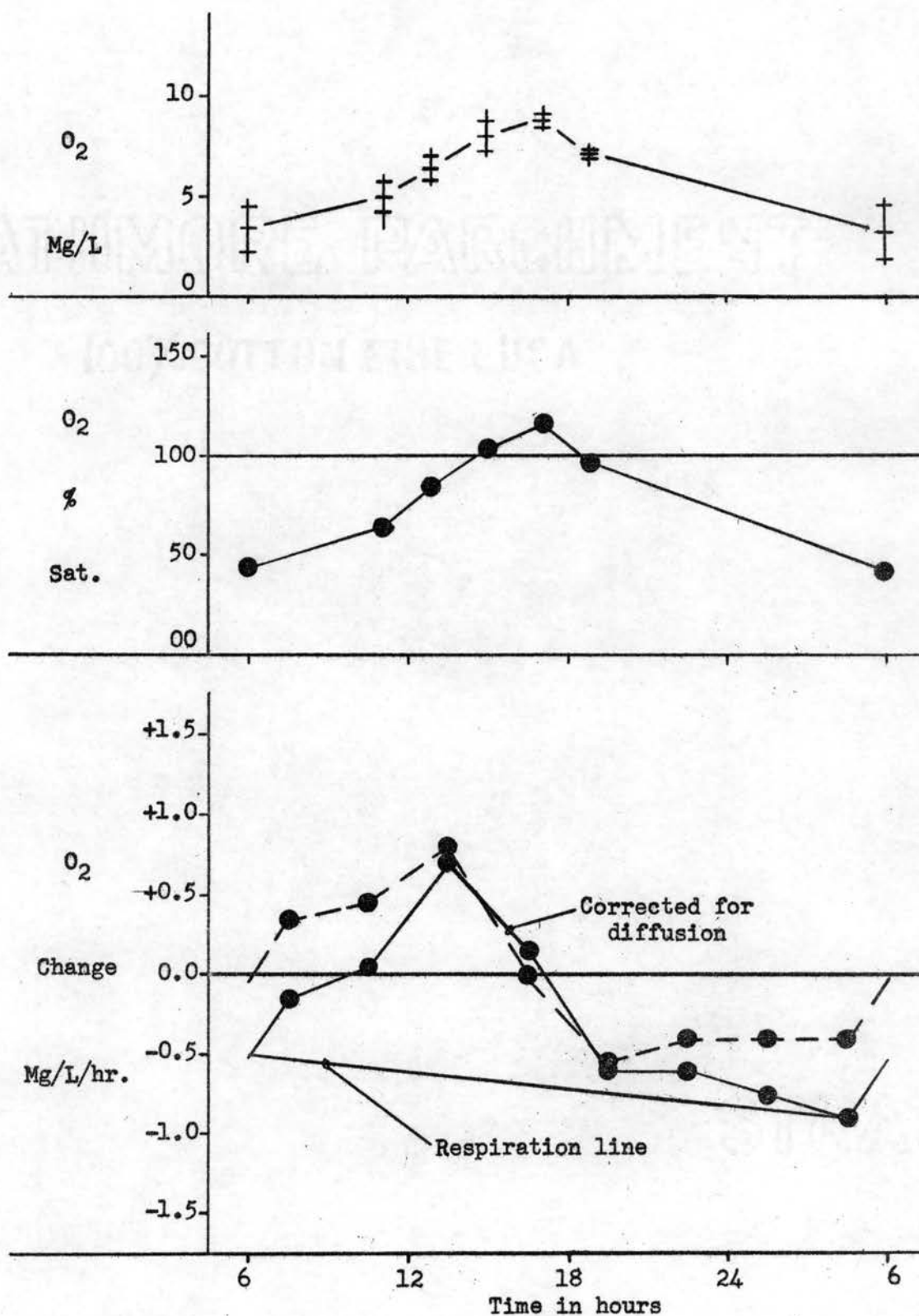


Figure 16: Diurnal oxygen curve for Bay 2 of Oxidation Pond #3 (26.0 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.



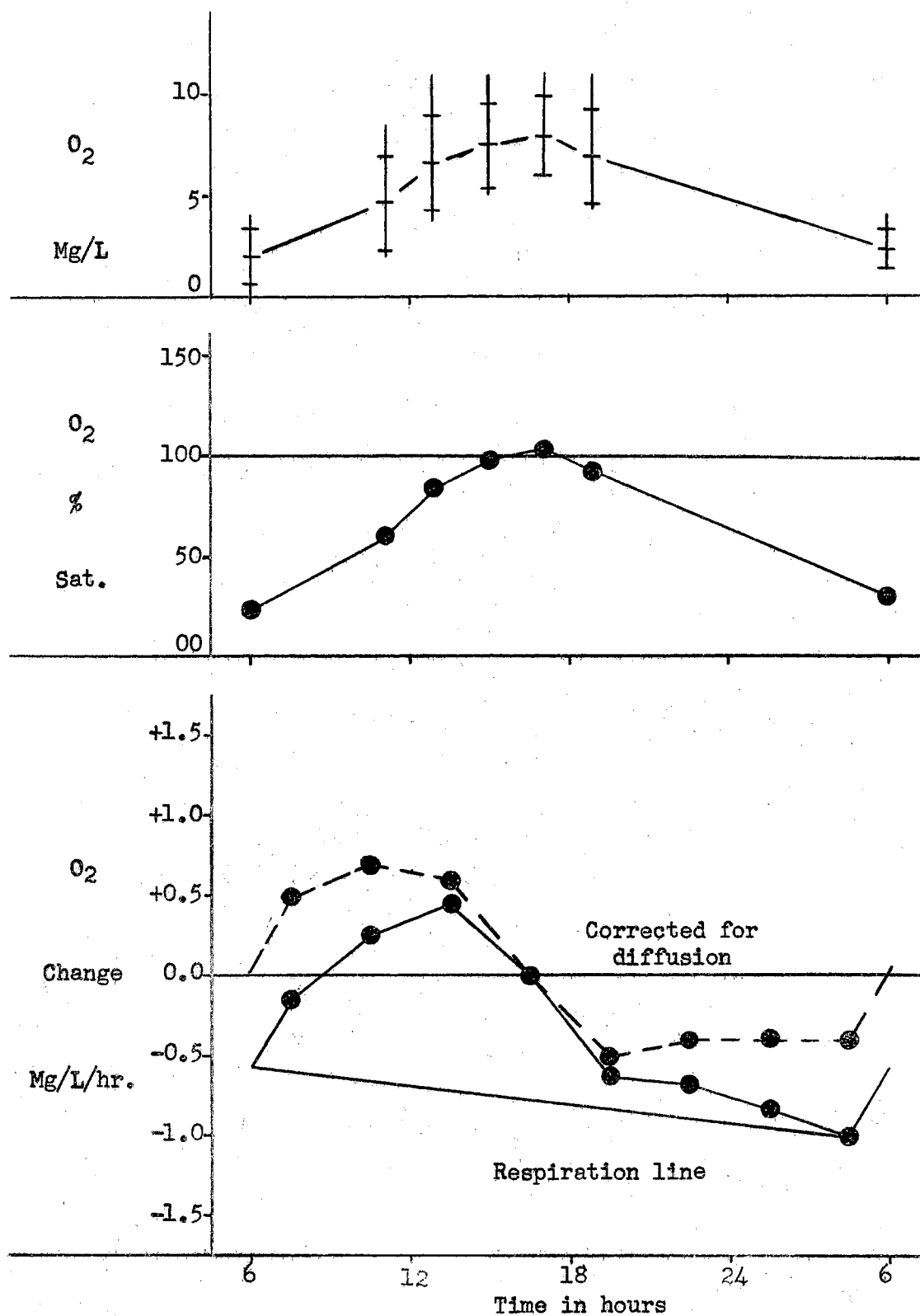


Figure 17: Diurnal oxygen curve for Bay 3 of Oxidation Pond #3 (31.0 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.

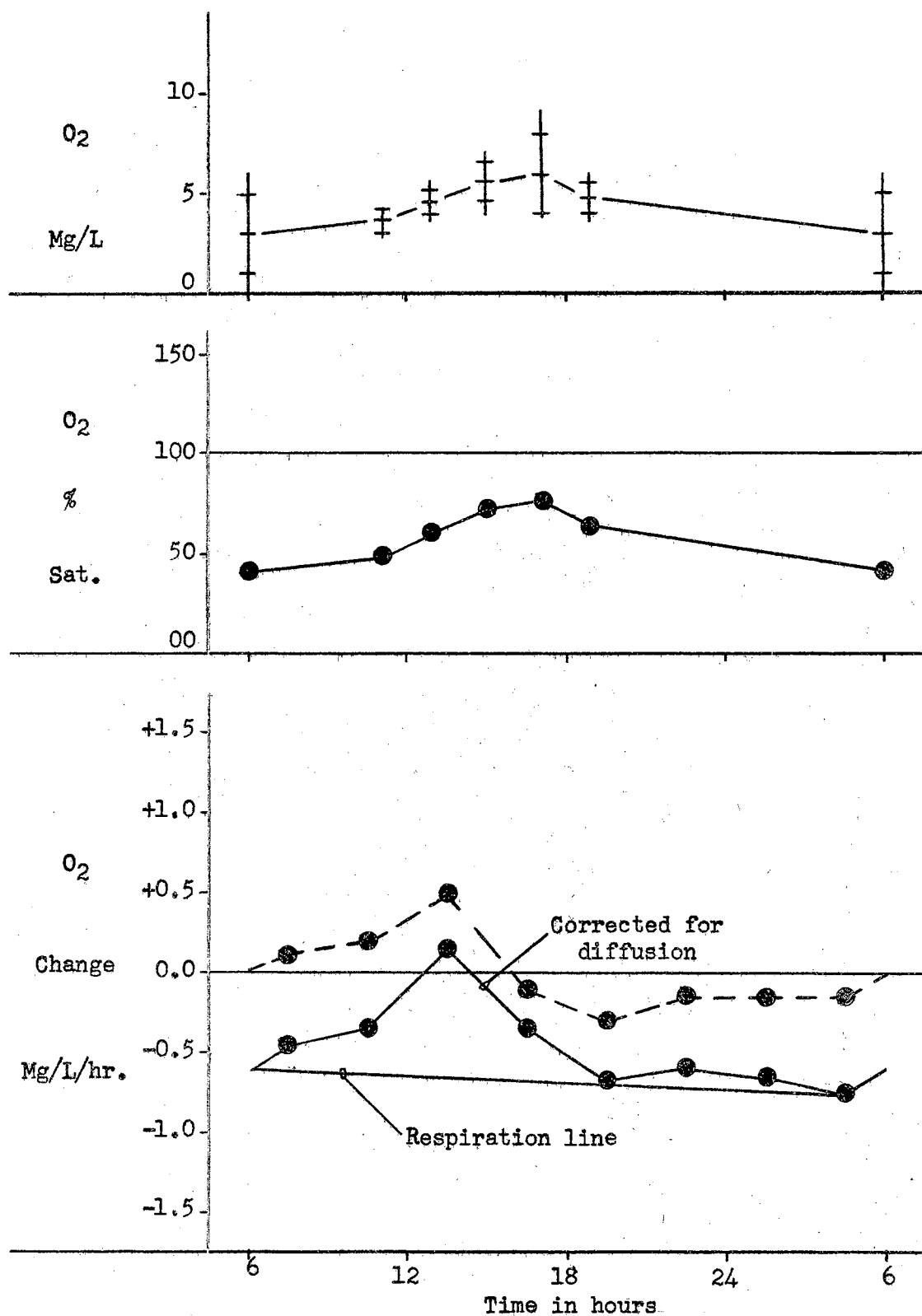


Figure 18: Diurnal oxygen curve for Bay 4 of Oxidation Pond #3 (37.0 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.

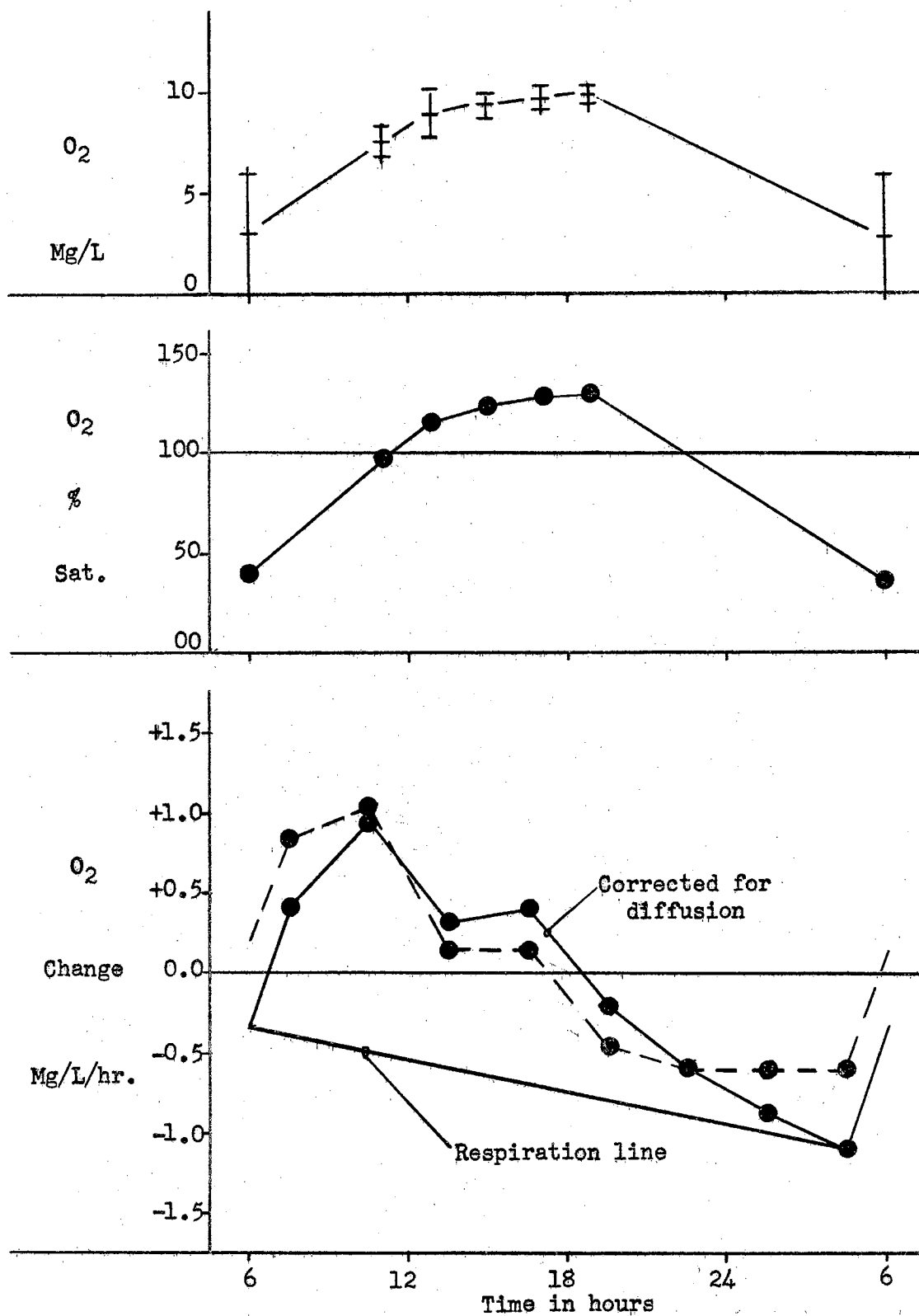


Figure 19: Diurnal oxygen curve for Bay 1 of Oxidation Pond #4 (48.0 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.

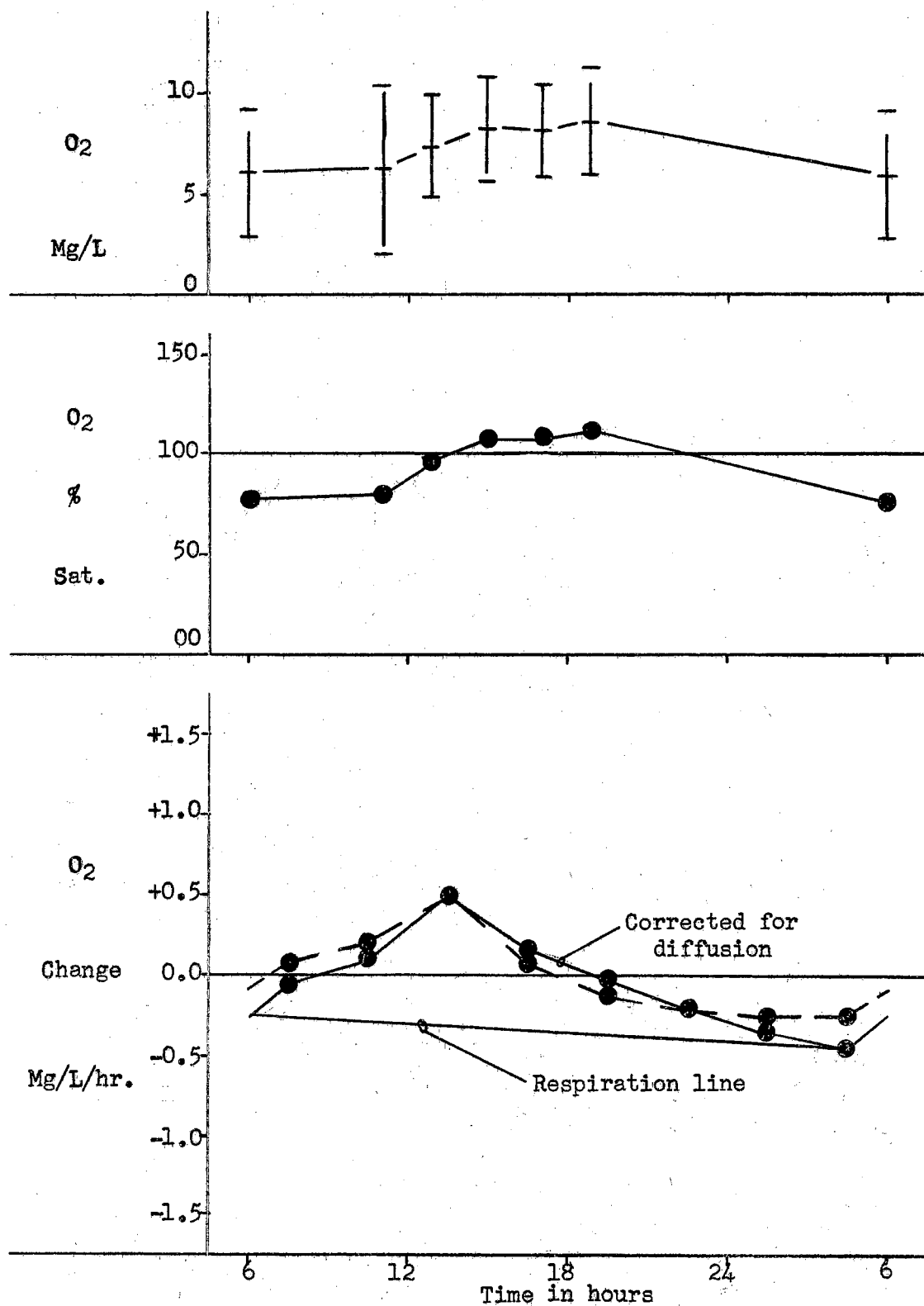


Figure 20: Diurnal oxygen curve for Bay 3 of Oxidation Pond #4 (60.4 days holding time) at Refinery B. See Figure 7 for the explanation of the uppermost curve.

VITA

Billy Joe Copeland

Candidate for the Degree of

Master of Science

Thesis: PRIMARY PRODUCTIVITY IN OIL REFINERY EFFLUENT-HOLDING PONDS

Major Field: Zoology

Biographical:

Personal Data: Born near Mannsville, Oklahoma, November 20, 1936, the son of William F. and Dorothy Mae Copeland.

Education: Attended grade school at Mannsville, Oklahoma; graduated from Mannsville High School in 1955; received the Associate of Science degree from Murray State Agricultural College, Tishomingo, Oklahoma, with a major in Agricultural Science, in May, 1957; received the Bachelor of Science degree from Oklahoma State University, with a major in Zoology, in May, 1959; completed requirements for the Master of Science degree in May, 1961.

Professional experience: Undergraduate research assistant under a National Science Foundation grant; graduate research assistant in the Zoology department; studied primary productivity of some Oklahoma reservoirs, chemical characteristics and pollution aspects of some Oklahoma oil refinery effluent-holding ponds during the summers of 1959 and 1960; co-author of a publication concerning the chemical characteristics of oil refinery effluent-holding ponds.

Member of: American Institute of Biological Science, American Society of Limnology and Oceanography, Ecological Society of America, Phi Theta Kappa, Phi Kappa Phi, Phi Sigma, Omicron Delta Kappa, and Oklahoma Academy of Science.